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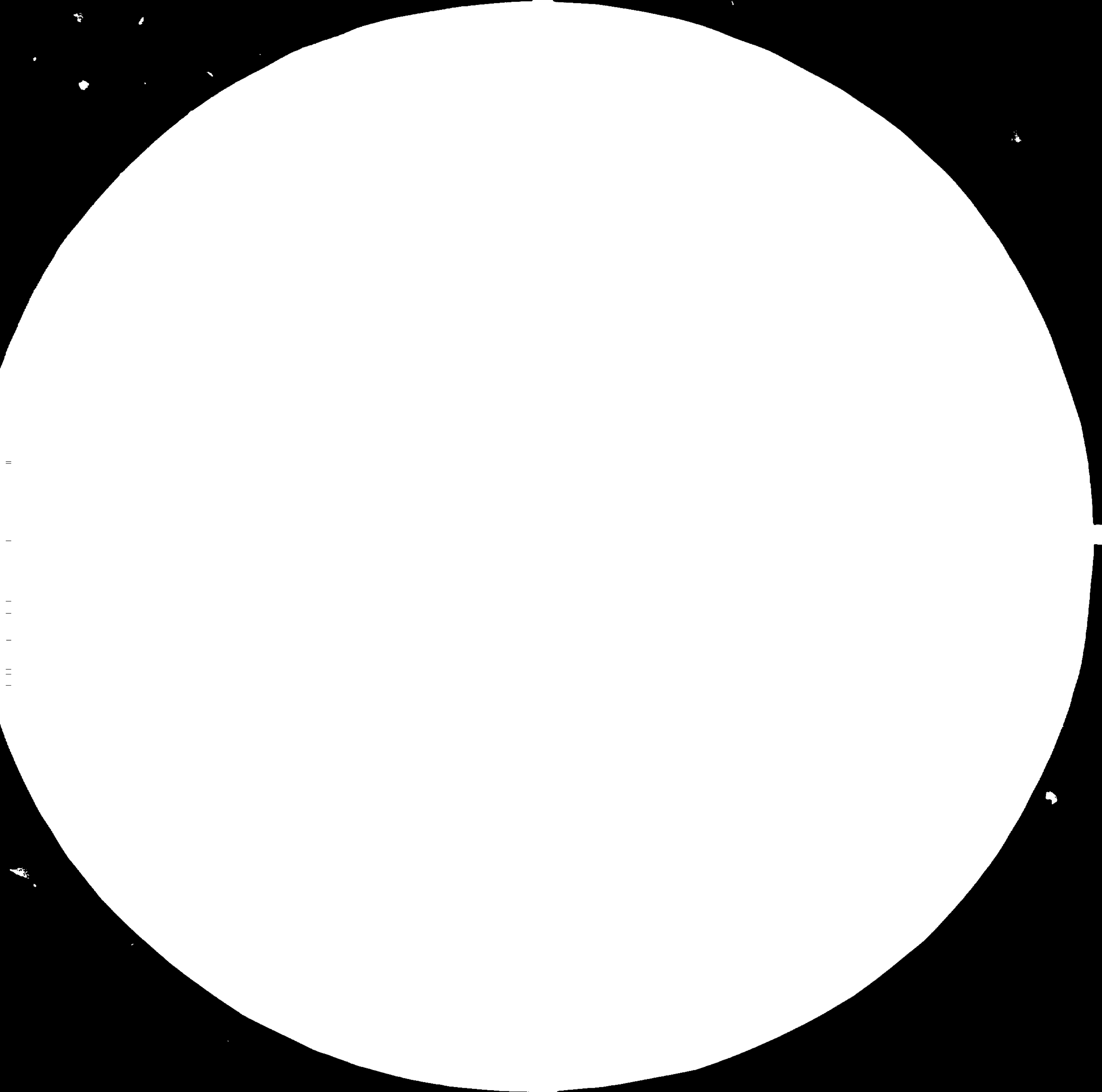

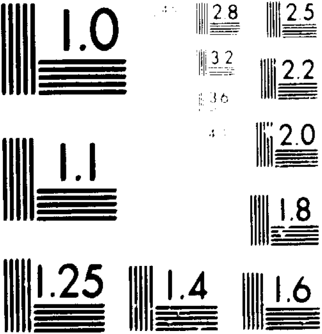

MICROCOPY RESOLUTION TEST CHART

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Confidential
Contract No. 79/29
Project No. US/RAS/77/016

11053
(1 of 2)

UNIDO Project
to Increase the Competitiveness of Natural Rubber

Final Report
January 1981

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MALAYSIAN RUBBER RESEARCH AND DEVELOPMENT BOARD

Confidential

Contract No. 79/29

Project No. US/RAS/77/016

UNIDO PROJECT
TO INCREASE THE COMPETITIVENESS
OF NATURAL RUBBER

FINAL REPORT

JANUARY 1981

from the Contractor

The Malaysian Rubber Research and Development Board

to

The United Nations Industrial Development Organization

CONTENTS

SYNOPSIS

Thermoplastic Natural Rubber Grafts

- The chemical route to azo-tipped polystyrene has been greatly simplified and cheapened to the point where the thermoplastic NR-polystyrene graft should be of similar cost to the synthetic thermoplastic block copolymers.
- The grafting operation has been successfully and routinely carried out in a Banbury internal mixer.
- The TPNR grafts have physical properties very similar to those of the synthetic block copolymers and may be compounded in the same way as the latter for specific applications or for cheapness.
- Two problems remain to be solved before semi-commercial operations can be recommended:- the influence of scale on the increased variability of polystyrene capping efficiency and the differences of grafting efficiency found with different batches of NR.
- The grafting route has been successfully applied to polyalphamethylstyrene and polymethylmethacrylate and there is little doubt that it could be extended to other polymers.

Thermoplastic Natural Rubber Blends

- TPNR blends of NR and polypropylene are now available on the tonnage scale.
- Physical properties and ageing behaviour of the TPNR blends are competitive with the range of TPR's based on EPDM.
- Formulations and blending procedures have optimised to give mouldings a good surface finish and appearance. An odour typical of NR products is the only remaining disadvantage

- TPNR will be cheaper than the EPDM blends especially in the NR producing countries, where production of TPNR blends for the manufacture of products for the domestic and export market should be initiated.

- Considerable promotional work and large scale trials with likely consumers has resulted in significant market interest in applications such as car bumpers and other automotive components, footwear, hoses, rail pads etc.

Powdered Natural Rubber

- Powdered or granulated NR is now available in bulk by several routes:- the spray-drying of latex; surface treatment (bromination) of crumb rubber; mechanical granulation of bale rubber.

- All these forms of powdered NR process readily in both conventional mixing equipment or in the new mixer-extruders designed for powder technology. The size of particles is unimportant up to 12 mm.

- Freight costs will make the export of powdered NR from NR-producing countries uneconomic. The use of powdered NR (probably brominated crumb) and modern powder-processing equipment in the rubber manufacturing industry of these countries could be advantageous.

- For use in consuming countries, mechanically ground NR produced 'in house' or by a custom granulator would be the recommended form of powdered NR. The premium over bale rubber it would carry has been calculated to range from £50/tonne (for 'in house' production) to £100/tonne.

- Detailed product cost calculations based on a new factory equipped with either conventional mixing equipment or powder mixing equipment of the same output indicate that at the present state of machinery development the cost savings arising from the use of powdered rubber will not generally offset the premium charged for this rubber.

1. INTRODUCTION

1.1 This project arose from an approach to UNIDO by the International Rubber Research and Development Board (IRRDB) suggesting that it would be of great value to the natural rubber (NR) producing countries if funds could be provided for a technological development project aimed at improving the future competitiveness of NR. Subsequently, a contract was entered into by UNIDO with the Malaysian Rubber Research and Development Board (MRRDB) acting as contractors for the IRRDB. The project work, started in February 1979, has been carried out at the MRRDB's two laboratories: The Rubber Research Institute of Malaysia (RRIM) and The Malaysian Rubber Producers' Research Association (MRPRA).

1.2 The objective of the Project is to increase the competitiveness of NR by developing new forms of NR which match presently available forms of synthetic rubbers and the future requirements of consumers. In the original submission by the IRRDB three new forms of NR were contemplated - thermoplastic NR, powdered NR, liquid NR - but in agreeing the content of the final Project it was decided that it would be preferable, for a number of practical reasons, to include only the first two of these.

1.3 For thermoplastic and powdered NR the work plans were drawn up in the light of the perceived state of the art at the time and on most effective routes to attainment of practical objectives within the time span (2 years) of the Project.

1.4 Inclusion of thermoplastic NR (TPNR) was on the basis that thermoplastic synthetic rubbers were displaying very rapid growth (ca 20 per cent/year) to the extent that they could eventually displace conventional forms of rubber in many types of application, and would also enable rubber (generically) to take on new applications Thermoplastic rubbers have a molecular architecture enabling them to behave at normal temperatures like vulcanized rubbers but to exhibit thermoplasticity at higher temperatures so that they can be shaped on the relatively simple machinery used to process thermoplastics such as PVC ; they offer considerable economies to the rubber products fabricator. In the case of NR the Project was based on two approaches for which preliminary work at MRPRA indicated a reasonable chance of success:

0 Materials based on comb-grafts of NR with polystyrene (TPNR grafts)

0 Materials comprising blends of NR with a polyolefin such as polypropylene (TPNR blends)

1.5 Inclusion of powdered NR was on the basis that for over a decade the world rubber industry has gone on record as stating that its future preference would be for rubber (natural or synthetic) in powdered/granulated form rather than in bales. This is in the belief that powdered rubber would provide economies (including saving of energy) which were more than sufficient to offset the premium that would need to be charged by the rubber producer. In fact, the use of powdered rubber (mostly synthetic) is still very small (about 1-2 per cent of total rubber) but the frequency and vigour of claims that it is the material of the future are such as to make it imperative that the technical and economic prospects for powdered NR be thoroughly examined. Since it is possible to produce powdered NR in either NR producing or consuming countries it was decided that the Project should evaluate both aspects.

2. THERMOPLASTIC GRAFT COPOLYMERS OF NR

Position at start of Project

2.1 Earlier work at MRPRA had established the basis of a method for the laboratory-scale preparation of NR/synthetic polymer graft copolymers the properties of which seemed likely to be similar to those of wholly-synthetic block copolymers of the styrene/butadiene/styrene class. The method was completely novel but, in its existing form, totally uneconomic. It involved (i) anionic polymerization of the chosen monomer, typically styrene, (ii) treatment of the resulting polymer with a series of reagents (involving several changes of solvent) to produce a polymer 'capped' with a reactive chemical grouping (azodicarboxylate), and (iii) formation of the TPNR graft copolymer by reaction with NR either in solution or in normal dry rubber mixing machinery. This latter option - formation of a thermoplastic rubber in the course of normal rubber processing - was seen as a uniquely advantageous feature.

Work plan

2.2 This comprised three main elements:

(i) thorough exploration of the chemical reactions required to produce capped polystyrene, including investigation of candidates other than the azodicarboxylate route, with the objective of developing an economically-viable reaction sequence,

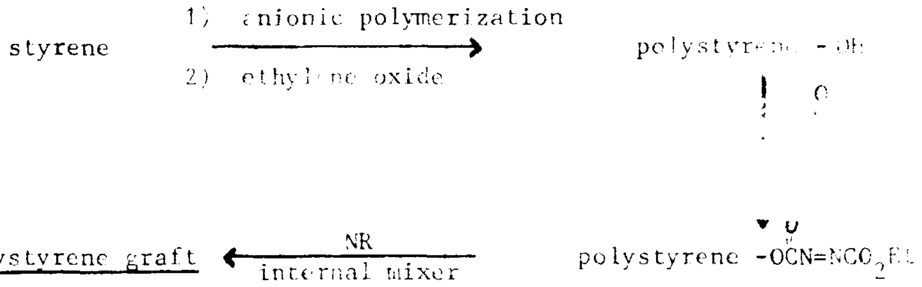
(ii) examination of polymers other than polystyrene,

(iii) selection of the most promising system for technological examination on a larger-than-laboratory scale, implying the need to scale up production to a reasonable level but below the pilot-plant level.

2.3 A fourth element in the original work plan - characterization of the relationship between molecular structure and properties - was judged to have a lower priority and characterization was limited to interpretation of normal technological properties.

Progress during Project

2.4 The original process - for styrene, with azodicarboxylate as the capping agent - has been greatly streamlined and simplified. Treatment of the polymer involves only one step instead of several (para. 2.1), preparation of the azodicarboxylate capping reagent being carried out separately. The route to graft copolymer can now be written as the following simple reaction sequence:-



Attention to every stage has enabled redundant quantities of many of the more expensive chemical reagents to be reduced to virtually theoretical levels ('full stoichiometry'). The effect that this has had on the economics can be summarized as follows. In order that the NR/polystyrene graft copolymer be price competitive with the similar wholly-synthetic block copolymer, the raw materials cost should total not more than about £[illegible]00/tonne of capped polystyrene (at current West European price levels). The original process had raw material costs of ca £2 500/tonne which were reduced by the route simplification to £1 300/tonne and thence to under £700/tonne by the improvements in stoichiometry. Thus, the process obtained by the end of the Project is regarded as being essentially cost-competitive in terms of raw materials.

2.5 The polystyrene graft was chosen as the most sensible candidate for larger-scale evaluation. The process for making capped polystyrene has been scaled up to 1.5 kg batches, enabling production of the TPNR graft to be achieved in a factory-type internal mixer, with reasonably comprehensive assessment of technological properties.

2.6 The possibilities of using capping agents other than azodicarboxylate have been examined: none shows any improvement.

2.7 Laboratory work has been carried out on grafting NR with polymers from methyl methacrylate and alphamethylstyrene. Synthesis of these polymers in suitable modified form is far less easy than is the case for styrene, and in the case of methyl methacrylate it was necessary to abandon anionic polymerization in favour of free radical polymerization (economically of considerable interest). The products from methyl methacrylate are tough, almost transparent materials which are thermoplastic graft copolymers.

Outcome

2.8 This part of the Project has created a thermoplastic form of NR which is technically very similar to comparable wholly-synthetic materials. Although certain properties of the TPNR graft are slightly inferior to those of the styrene/butadiene/styrene block copolymers the differences are unlikely to be significant in practical applications. When NR is replaced by synthetic polyisoprene physical properties become poorer which is fortunate as this grafting route is obviously applicable to such competitors.

29 Since neither the time scale nor the terms of reference of the project permitted examination of just how a full-scale process might be operated, the only possible estimate that can be made of likely production cost is via raw materials costs. The indication is that, provided scale-up to a production process poses no unexpected problems, the polystyrene copolymer could be competitive with the comparable wholly-synthetic material.

Problems relevant to further implementation

2.10 Two problems need to be solved before serious consideration could be given to larger-scale production: One is that the high degree of functionality of the polystyrene achieved in the capping process carried out on the small scale becomes more variable as the scale increases. It is thought that this is due to the greater difficulty of work-up and isolation which would probably disappear in a properly engineered industrial process. The second is the variation in the efficiency of grafting during dry mixing from one batch of NR to another and almost certainly due to the variable presence of non-rubber substances. Various means have been found for mitigating their influence but it cannot yet be said that a high level of grafting with each and every batch of market-grade NR can be guaranteed.

2.11 Given that it is subsequently decided to scale-up the process there will undoubtedly be many chemical engineering problems to be tackled in addition to those concerned with anionic polymerization on the large scale. For example, in the laboratory-scale preparation the capped polymer is 'worked up' by precipitation from solution; this would be totally uneconomic for full-scale production and it would be necessary to use the kind of methods used in the production of, for example, solution-polymerized synthetic rubbers (eg steam stripping). As noted (para 2.9) such activity was outside the scope of the Project, but it is as well to emphasize its importance.

3. THERMOPLASTIC NATURAL RUBBER BLENDS

Position at start of Project

3.1 Originally it was believed that a thermoplastic rubber would need to be a copolymer or graft of a hard plastic and a rubber in which rubber chains were 'crosslinked' at ambient temperatures by domains of the hard material. More recently, there has come onto the market a number of thermoplastic rubbers which are simple physical blends, mostly based on the synthetic rubber EPDM and a polyolefin such as polypropylene. Such materials are 'different' from the copolymer thermoplastic rubbers and are simpler and cheaper to produce: they tend to be harder than typical rubbers, and represent a half-way house between plastics and true rubbers. They have already established fast-growing markets in automotive body components (eg bumpers) and their success in these is leading to wider usage in a variety of moulded and extruded products.

3.2 Recognizing the desirability of establishing a niche for NR in this expanding market, MRPRA had previously carried out a brief feasibility study. This showed that TPNR blends appeared to match the overall properties of wholly-synthetic blends: they could readily be moulded (eg by injection moulding); their stiffness could be adjusted by varying the blend composition; they could readily be painted (an important consideration for the main applicational area envisaged: automotive body components) and ageing behaviour was excellent even on exposure to ozone.

Work plan

3.3 The official work plan had only one requirement: 'optimization of blends of NR with synthetic thermoplastic materials'. This has been interpreted as requiring:

(i) devising blend formulations particularly of NR and polypropylene suitable for a variety of likely applications,

(ii) demonstration of feasibility of large-scale production,

(iii) assessment of the economics,

(iv) stimulation of interest among potential users.

Progress during Project

3.4 In the light of knowledge concerning current applications of the wholly-synthetic blends a number of applicational areas for TPNR blends have been identified, and blend compositions have been developed to meet the requirements (specified or inferred) for these.

3.5 Considerable experience has been gained relevant to the large-scale factory production of TPNR blends, culminating in production trials (50 kg batch weight) in the factory of a UK custom compounder. Production has also been carried out by the RRIM in Malaysia. The blending operation, in a standard rubber internal mixer, is simple and no problems have been encountered. There is no obstacle, therefore, to tonnage scale production of TPNR blends. Experience has also been gained on the subsequent processing stages (eg injection moulding) with a variety of processing machines. Again, no problems are foreseen: as is always the case with new materials it is simply a matter of learning how to optimize the processing conditions to suit the material.

3.6 Estimates of production cost in the West (specifically in the UK), confirmed by discussions with the UK company noted in para. 3.5, indicate that the commercial selling price for TPNR blends could undercut that for comparable synthetics by 15-20 per cent. Estimates of production cost in an NR producing country (specifically Malaysia) show the expected influence of lower labour and depreciation charges and the lower cost of NR (duty remission and absence of freight costs) make the overall competitive position of TPNR blends even more attractive.

3.7 Considerable interest has been aroused in a number of applicational areas. The main promotional effort has been on automotive components, including production trials for the bumpers of a Scandinavian car. Footwear (soling) is another promising area and it is significant to note that the RRIM was successful in persuading an international footwear company to put the RRIM-produced TPNR blend (para. 3.5) into production trials for its local operation. Other applications currently undergoing development include: rail pads (under test by a European railway network); linings for chemical plant (an international chemical company has accepted a TPNR blend as meeting their specification for chemical resistance); products for the dairyindustry; stair nosings and irrigation hose.

Outcome

3.8 TPNR blends have been developed to the stage where large-scale production and use is feasible; blend compositions can readily be tailored to meet the needs of individual applications and processing conditions. TPNR blends could be produced very economically in the West (ie from imported NR), though it should be said that this will probably not apply in the USA where governmental policies concerning oil prices cause the prices for all plastics and synthetic rubbers to be low by world standards. Export of TPNR blends from NR producing countries can certainly be considered, and of course the material would be of exceptional interest for domestic use in those NR producing countries which are actively encouraging local manufacture of plastics and rubber products for which TPNR blends could readily compete with imported synthetic materials.

Problems relevant to further implementation

3.9 These are minor. In some circumstances TPNR blends have an unpleasant odour, more significant during processing than in use. This can be ameliorated in various ways but may be a disqualifying factor where odour is totally unacceptable. Some problems have also been found in contriving a satisfactory surface appearance of mouldings, but these have been overcome after detailed adjustments to blend composition and/or processing conditions.

4. POWDERED NATURAL RUBBER

Position at start of Project

4.1 As hinted at in the Introduction (para. 1.5), there is a fundamental hesitancy concerning the future of powdered rubber: despite strident assertions as to its potential, very little is actually used and of this the bulk is special-purpose synthetic rubbers. For NR, there is only one commercial manufacturer in an NR producing country (Malaysia), who obtains a fine powder by spray-drying latex, the use of which is limited mainly to the preparation of rubber solutions for adhesives (fast dissolution); output is a few hundred tonnes/year, probably only 10 per cent of plant capacity. Other than that, the only NR used in powder/granule form is that which is custom-granulated from bales in consuming countries, either in-house or by companies which specialize in this; the quantity involved is certainly less than 1 per cent of NR consumption.

4.2 Within the research institutes of IRRDB member countries there was virtually no knowledge of nor expertise on powdered NR, and the driving force behind inception of this part of the Project was to fill this information gap so that the NR producing countries could be better placed to take advantage of the purported future potential for powdered NR.

Work plan

4.3 There were four elements:

(i) production and evaluation of experimental types of powdered NR,

(ii) development of processing techniques using conventional and special machinery,

(iii) development of formulations,

(iv) study of the economics of production and transport.

Progress during Project

4.4 Several production routes have been investigated of which the most promising on economic and technological grounds are brominated crumb NR and mechanically-granulated NR. The former process was invented during the course of the Project to meet the requirement that NR producers should be able to make free-flowing NR directly from latex. Mechanical granulation is not novel but its simple practicality suggested that experience in its use needed to be gained and it provides a convenient means for examining variables such as particle size and partitioning agent and for producing bulk quantities for large scale processing trials.

4.5 Whatever process is used it is necessary to prevent re-agglomeration of particles during production and transport. Normally this is done by incorporating a 'partitioning agent', typically talc or silica. An alternative approach is chemically to treat the surface of the NR particles in some way so as to make them less tacky. As far as is known, this has not previously been tried and the method devised for the Project is novel. It involves treatment with bromine in solution, and preliminary experiments showed that the procedure was feasible. Subsequently a pilot plant was set up at the RRIM in Malaysia. The granules produced travel well with little re-agglomeration and the material processes adequately, but the overall cost of the process is higher than that of mechanical granulation (especially since it was later found necessary to use longer-than-expected drying times).

4.6 Mechanical granulation of NR in bale form is the standard method used by 'custom granulators' in the West but there is virtually no information available to NR producers on how best to carry out the process. This information gap has been filled, using the standard commercial granulator installed as part of the Project equipment, and much useful data has been obtained on features such as optimum particle size, throughput under various conditions, choice of partitioning agent, and so on. Also, the machine has been used to provide material for processing trials.

4.7 Using material from the granulator, trials of processing performance have been carried out in conventional internal mixers and in two of the newly-available powder processing machines: 'mixer-extruders' equipped with vacuum venting to remove entrapped air and volatile substances. Such machines can accept material from a powder blender and produce a precision extrudate ready for vulcanization. During the trials, particular attention was paid to energy usage in view of claims made on this point: with the internal mixer there is some small saving of energy (4-12 per cent) and there is also some saving with the mixer-extruders, though this seems to be associated with high extrudate viscosity and poor dispersion, and production of better-quality extrudates may eliminate the energy saving. A trial was also carried out on the direct injection moulding of granulated NR, using a machine devised specifically for this; the results were only moderately satisfactory. Overall, the impression gained is that a good deal of work will need to be done by machinery manufacturers and rubber producers before the processing of powdered rubber on the new machines will approach the predictability and versatility of conventional processing of bale rubber.

4.8 Sufficient experience has been gained in formulating mixes for various situations to be reasonably confident that the procedures needed are well understood. In fact, devising formulations for powdered rubber processing involves nothing more than the intelligent application of standard rubber technology, eg attention to features such as 'scorch safety', although it has to be recognised that processing conditions in mixer-extruders are less flexible than in conventional machinery.

4.9 It is in the area of costs that the real problem arises. Estimates have been made of the likely cost of production by various processes in Malaysia, and by mechanical granulation in the UK. The cheapest of the three Malaysian processes assessed is 'talced crumb', made simply by adding talc to NR during its comminution in the normal block rubber process (a process formerly operated on a modest commercial scale). The factory cost, extra to that of the starting NR, is low (£27/tonne) but unfortunately the material is not commercially viable because its storage life (re-agglomeration) is too short for export and probably for domestic use. Spray-dried latex (para. 4.1) is the most expensive (£124/tonne) and the new brominated crumb process (para. 4.5) was originally costed at £72/tonne but this must now be increased to allow for extra drying time. For all three forms, since their density is about one-half of that of bale NR, and since freight is charged on a volume basis, there is a substantial extra cost for ocean and land freight, plus insurance, assessed at about £70/tonne. Thus, there is no viable technology at present capable of landing powdered NR in a consuming country at a premium over bale NR much less than about £150/tonne which, as will be shown (para. 4.10) is far too high. Brominated crumb, though, is a possible candidate for domestic use in NR producing countries. For mechanical granulation in a consuming country the extra cost ranges from about £50/tonne for 'in-house' granulation (no freight, packaging or working capital charges) to around £100 for 'custom granulation'; these estimates are in line with commercial prices in the UK.

4.10 Estimates have been made of total production costs of (a) unvulcanized strip and (b) a continuously vulcanized finished extrusion in a new factory equipped with conventional Banbury mixers using bale rubber or with MVX mixer-extruders using mechanically comminuted rubber at a premium of £100/tonne. This suggests for (a) a cost disadvantage for the powdered route of £30 - £80/tonne of product depending on the assumptions made of MVX output. For (b) a cost disadvantage of £35/tonne under likely output conditions could become a break-even situation with the most optimistic output assumptions. The cheaper 'in house' cost of granulation mentioned in 4.9 will affect the picture but it is clear that at the present stage of development of powdered rubber processing machinery the processing cost advantage of the powder route does not normally offset the premium charged for the powdered NR. As the processing machinery develops with higher outputs relative to capital charges/labour costs then the use of powdered rubber may become more attractive.

Outcome

4.11 Several routes (spray-dried latex, brominated crumb rubber, mechanically ground rubber) are available for the large scale production of powdered NR if consumers require this. However, it has not yet proved possible to devise a form of powdered NR which is economically viable for export from NR producing countries. Given the small processing cost advantage that a consumer will see (which will be reflected in the premium he is prepared to pay) and given the high extra cost of freight, attainment of this objective will be very hard. For domestic use in NR producing countries this part of the Project has yielded some valuable leads. Brominated crumb is a candidate for domestic use, and it is also possible that some of the information on mechanical granulation could be adapted for the conditions in NR producing countries (where clearly it would not make sense to produce NR in bales for subsequent granulation). As the rubber manufacturing industry expands in the producing countries the design of new factories around powdered rubber processes may well be advantageous for certain products.

4.12 Perhaps the most useful outcome has been clarification of the 'powdered rubber problem' - underlining of the fact that this is neither a fast-growing market nor an easy option for the NR producers.

Problems relevant to further implementation

4.13 Assuming that the main objective ultimately is to devise an exportable form of powdered NR the main problem is that of the high extra freight associated with low-density powder or granules. What is needed is a way of temporarily aggregating NR particles in such a way that their density for transport is greatly increased; subsequent easy dis-aggregation in the consumer's factory will be essential.

5. DISCUSSION

5.1 It can justifiably be claimed that the Project - taken as a whole - has yielded information of material value to the overall objective: increasing the competitiveness of NR by developing new forms.

5.2 A point that has not yet been explicitly made is that the rubber industry in the NR producing countries comprises two facets: production of raw NR for export, local use to make rubber products both for import substitution purposes and for export. New forms of NR are relevant to both. Export of a new form of NR of higher added-value than normal NR is clearly beneficial. So also is the production and local use of such a new form, and indeed in a wider context (eg the New International Economic Order) this facet might well be regarded as being of greater long-term significance. In developing this Project both facets have been kept in mind, but with a feeling that local production and use of the new forms is what is ultimately the more desirable.

5.3 An immediately tangible outcome of the Project is a viable form of thermoplastic NR - the TPNR blends described in Section 3 which have been taken to the point of commercial feasibility. These can readily be produced in any country of the world which has access to NR and to polyolefins at sensible prices, and the NR producers could not prevent such production. In fact, there is no reason why they should not encourage it; it is after all a way of extending the utility (and hence the price) of NR More important, though, is for the NR producing countries to encourage production of TPNR blends in their own countries (para. 3.8) for export as such or, more valuably, for product manufacture for the home market and export.

5.4 Development to the point of commercial take-off of the other form of TPNR - the graft copolymers described in Section 2 - was not envisaged within the time-scale and terms of reference of the Project. In fact, considerable and useful progress has been made in what is an exceptionally difficult area and the process is now ready for pilot plant scale up. Under what circumstances should it be taken further? It is highly unlikely that industrialized consuming countries will be interested in undertaking production of such materials: they will generally be better placed to exploit all-synthetic routes. NR producing countries should consider investment of time and effort in this area only if they have - or intend to develop - a substantial chemicals/ petrochemicals industry, and even then they must expect to find that chemical engineering scale-up of the process will not be easy. It must also be said that, although the polystyrene-grafted system was selected for the main effort on the basis of existing know-how and likely chance of success, it is unlikely that this system will prove to be the most important in the long run. Copolymers with other components may be able to provide valuable features that are not obtainable with the current styrene/butadiene/styrene synthetics but, although some work along these lines has been carried out (para. 2.7), more is needed.

5.5 In connexion with powdered/granulated forms of NR the word 'hesitancy' was used (para. 4.1) and the point has been made that the most useful outcome of this exercise has been the underlining of this impression. This may seem a negative outcome but, just as it is important that the NR producing countries should be assisted to exploit real opportunities, so equally is it important that they be helped to avoid wasting effort on a chimera. Published statements concerning the prospects for powdered rubbers are mostly misleading or, in some cases, refer to special rather than to general situations. There is a market for powdered rubbers, but is is small and growing slowly. Probably it will accelerate only if and when new types of powder processing equipment become available at low prices (relative to internal mixers) and with greater versatility.

5.6 What should be the strategy of the NR producing countries in the meantime? They should essentially adopt a 'wait and see' policy, but making sure that they are aware of the latest technical trends affecting powdered rubber usage so that they can keep NR technology matched to these trends, ready to move into large-scale action when the opportunity is ripe. Meanwhile the rubber products manufacturing sector in those countries should examine very carefully those cases where powdered rubbers are being used effectively in the main consuming countries, to identify precisely the reasons why, and to investigate - in liaison with local NR producers - the desirability of developing similar areas of domestic powdered NR usage. This option also takes care of the problem that export of all known forms of powdered NR will always come against the problems of high freight costs - unless some new form can be devised (para. 4.12). Of course, in situations where consumers in developed countries wish to use locally-granulated NR it makes good sense for the NR producing countries to advise and assist - and the current exercise has provided useful data for this purpose.

6. RECOMMENDATIONS

6.1 From the foregoing discussion the following brief recommendations are made concerning actions that could be taken by the NR producing countries:

* The NR producing countries should actively consider establishment of facilities for the production of thermoplastic NR blends, for export as such and for use by local product fabricators.

* Further development of chemical routes to thermoplastic graft copolymers of NR should only be considered by those NR producing countries which are developing a comprehensive chemicals/ petrochemicals industry and with due regard to the chemical engineering complexities involved.

* The attitude of the NR producing countries towards powdered/granulated forms of NR should be one of caution, avoiding premature investments in an uncertain area. Modest development of the use of powdered NR and powdered rubber processing equipment in their expanding rubber manufacturing industry could provide a useful competitive edge for the export of certain products.

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UNIDO Project

to Increase the Competitiveness of Natural Rubber

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1 GENERAL INTRODUCTION

1.1 This project arose from an approach to UNIDO by the International Rubber Research and Development Board (IRRDB) suggesting that it would be of great value to the natural rubber (NR) producing countries if funds could be provided for a technological development project aimed at improving the future competitiveness of NR. Subsequently, a contract was entered into by UNIDO with the Malaysian Rubber Research and Development Board (MRRDB) acting as contractors for the IRRDB. The project work, started in February 1979, has been carried out at the MRRDB's two laboratories: The Rubber Research Institute of Malaysia (RRIM) and The Malaysian Rubber Producers' Research Association (MRPRA).

1.2 The objective of the Project is to increase the competitiveness of NR by developing new forms of NR which match presently available forms of synthetic rubbers and the future requirements of consumers. In the original submission by the IRRDB three new forms of NR were contemplated - thermoplastic NR, powdered NR, liquid NR - but in agreeing the content of the final Project it was decided that it would be preferable, for a number of practical reasons, to include only the first two of these.

1.3 For thermoplastic and powdered NR the work plans were drawn up in the light of the perceived state of the art at the time and the most effective routes to attainment of practical objectives within the time span (2 years) of the Project.

1.4 Inclusion of <u>thermoplastic NR</u> (TPNR) was on the basis that thermoplastic synthetic rubbers were displaying very rapid growth (ca 20 per cent/year) to the extent that they could eventually displace conventional forms of rubber in many types of application, and would also enable rubber (generically) to take on new applications. Thermoplastic rubbers have a molecular architecture enabling them to behave at normal temperatures like vulcanized rubbers but to exhibit thermoplasticity at higher temperatures so that they can be shaped on the relatively simple machinery used to process thermoplastics such as PVC; they offer considerable economies to the rubber products fabricator. In the case of NR the Project was based on two approaches for which preliminary work at MRPRA indicated a reasonable chance of success:

- 0 Materials based on comb-grafts of NR with poly(styrene) (TPNR grafts)
- 0 Materials comprising blends of NR with a polyolefin such as poly(propylene) (TPNR blends)

1.5 Inclusion of powdered NR was on the basis that for over a decade the world rubber industry has gone on record as stating that its future preference would be for rubber (natural or synthetic) in powdered/granulated form rather than in bales. This is in the belief that powdered rubber would provide economies (including saving of energy) which were more than sufficient to offset the premium that would need to be charged by the rubber producer. In fact, the use of powdered rubber (mostly synthetic) is still very small (about 1-2 per cent of total rubber) but the frequency and vigour of claims that it is the material of the future are such as to make it imperative that the technical and economic prospects for powdered NR be thoroughly examined. Since it is possible to produce powdered NR in either NR producing or consuming countries it was decided that the Project should evaluate both aspects.

As the three essential parts of the Project (TPNR Grafts, TPNR Blends and Powdered NR) are so distinct from one another each will be reported upon quite separately.

2 THERMOPLASTIC GRAFT COPOLYMERS OF NR

2.1 INTRODUCTION

2.1.1 Concept

An important class of synthetic thermoplastic rubber finding industrial application is the ABA block copolymer where A is a block of a hard plastic, typically poly(styrene), placed at each end of a rubber block B, typically poly(butadiene). Such block copolymers cannot be readily derived from natural rubber.

It has recently been demonstrated that copolymers in the form of short side chains of a hard plastic regularly spaced on the backbone of a rubber can exhibit the thermoplastic behaviour of a block copolymer. One method of preparing such materials from NR involves the concept of the plastic chains being presynthesised with exactly one terminal group which is highly reactive towards NR and which will allow grafting to occur in solution or, preferably, during dry mixing of NR with the reactive polymer.

2.1.2 Implementation

Work under this section of the Project has proceeded via the following stages to bring the theoretical concept to a practical reality.

(i) The establishment of a chemical route whereby poly(styrene) of accurately controlled molecular weight prepared by anionic polymerization can be capped with a group highly reactive to NR to a high degree of monofunctionality. Out of the several capping groups considered, azodicarboxylate was chosen as the most useful overall. The azo-capped poly(styrene) has good long term stability at ambient temperature.

(ii) The demonstration that azo-poly(styrene) grafts efficiently to NR during a simple dry-mixing operation in an internal mixer. Grafting can be 100 per cent of theory with a pure rubber but is reduced to a normal value of 70-75 per cent of theory by interference of the non-rubbers in NR.

(iii) The grafted product was shown to be a thermoplastic rubber with optimal physical properties at particular poly(styrene) contents and molecular weights. At these optimum levels the physical properties were very similar to those of typical commercial thermoplastic block copolymers.

(iv) A detailed examination of the chemistry of synthesis of the azo-poly(styrene) enabled a greatly simplified route to be devised. This, together with the use of cheaper reagents and solvents in as near stoichiometric amounts as possible, has reduced the raw materials cost by over three-fold virtually to the target figure of £600/tonne calculated to make the TPNR grafts cost competitive with synthetic block copolymers.

(v) The synthesis of azo-poly(styrene) has been scaled up to the limits of the laboratory anionic polymerization equipment (1.5 kg batches) to enable dry-mixing grafting and compounding studies to be carried out using a reasonably sized Banbury mixer.

(vi) Preliminary work has shown that the concept can be successfully extended to the preparation of graft copolymers of NR with poly(methylmethacrylate) and poly(alphamethylstyrene).

2.1.3 Outcome

The synthesis of the NR-poly(styrene) comb grafts has generated a thermoplastic form of NR which is technically very similar to comparable wholly-synthetic materials. Although certain properties of the TPNR graft are slightly inferior to those of the styrene/butadiene/styrene block copolymers the differences are unlikely to be significant in practical applications, where further compounding is usually involved. When NR is replaced by synthetic poly(isoprene) physical properties become poorer which is fortunate as this grafting route is obviously applicable to such a competitive material. Since neither the time scale nor the terms of reference of the project permitted examination of just how a full-scale process might be engineered and operated, the only possible estimate that can be made of the likely production cost is via raw materials costs. The indication is that, provided scale-up to a production process poses no unexpected problems, the NR-poly(styrene) grafts could be competitive with the comparable wholly-synthetic material.

2.1.4 Problems relevant to industrial implementation

Two problems need to be solved before serious consideration could be given to larger-scale production: One is that the high degree of functionality of the poly(styrene) achieved in the capping process carried out on the small scale becomes more variable as the scale increases. It is thought that this is due to the greater difficulty of work-up and isolation which would probably disappear in a properly engineered industrial process. The second is the variation in the efficiency of grafting during dry mixing from one batch of NR to another and almost certainly due to the variable presence of non-rubber substances. Means have been found for mitigating their influence but it cannot yet be said that a high level of grafting with each and every batch of market-grade NR can be guaranteed.

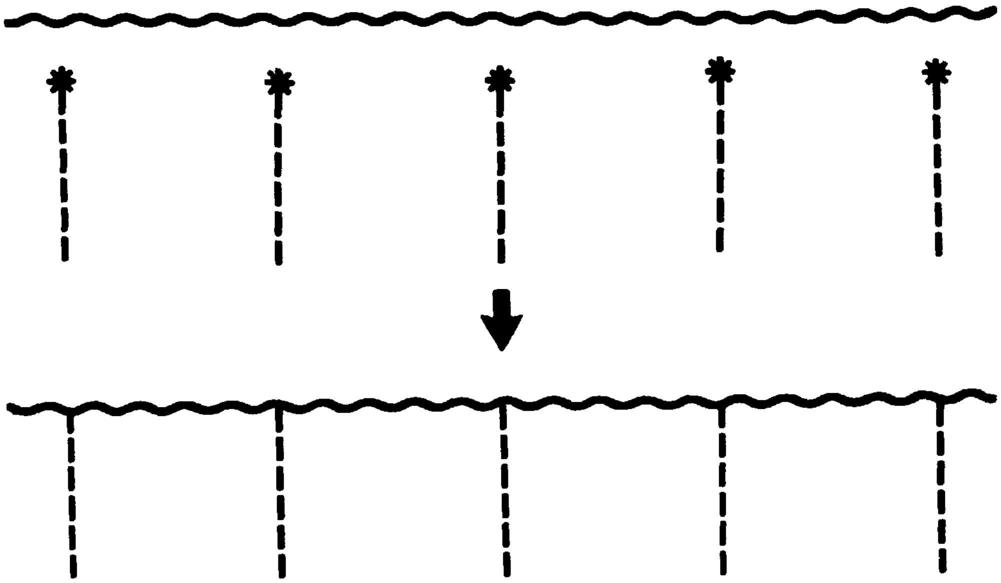
In any industrial scale-up of the process there will undoubtedly be chemical engineering problems to be tackled in addition to those concerned with anionic polymerization on the large scale. For example, in the laboratory-scale preparation the capped polymer is isolated by precipitation from solution; this would be totally uneconomic for full-scale production and it would be necessary to use the kind of methods used in the production of, for example, solution-polymerized synthetic rubbers (eg steam stripping). Such activity was outside the scope of the project, but it is as well to emphasize its importance.

2.2 BODY OF REPORT (THERMOPLASTIC GRAFTS)

2.2.1 Concept of comb grafts of NR

Very considerable industrial interest has been aroused by the thermoplastic rubber behaviour of the ABA block copolymers where the A blocks may be poly(styrene) of molecular weight 10-20 000 and the B block is poly(butadiene) of molecular weight 50-100 000. The direct imitation of such a structure starting from NR presents very formidable chemical problems. However, it has been shown (Falk et al, Rubb. Chem. Technol., 1973, 46, 1044) that a comb graft in which 'teeth' of poly(styrene) of molecular weight about 3 000 were grafted along a poly(diene) chain with an average molecular weight between 'teeth' of about 6 000 gave a product with thermoplastic rubber properties very similar to those of the block copolymers. The method they employed was carbanionic polymerization of styrene from metallated centres on the poly(diene) in solution and is not applicable to NR.

The principle adopted to arrive at comb grafts of NR involved the synthesis of the 'teeth', for example poly(styrene), of the correct molecular weight, equipped with a reactive end group capable of becoming attached to the NR backbone when the two polymers were mixed as illustrated in the figure below. The average spacings between the 'teeth' could be regulated by the weight added of poly(styrene) of any fixed molecular weight.



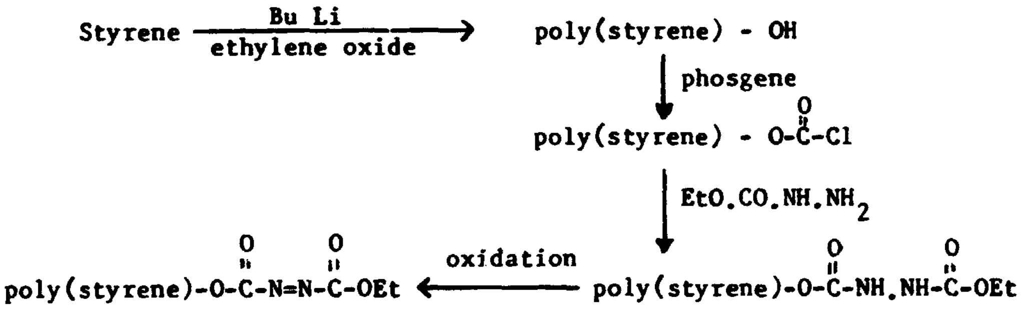
Obviously the successful use of this principle depends on several factors:- the identification of a suitable reactive terminal group, a chemical route to introduce the group on to one end only of anionically polymerized poly(styrene) and the ability to graft the reactive poly(styrene) on to NR under simple mixing conditions as grafting in solution would be quite uneconomic.

2.2.2 The route to a suitably capped poly(styrene)

The choice of capping group was critical to the successful outcome of the concept. Requirements included that the group be stable at room temperature for a good shelf-life of the capped poly(styrene), be efficient and rapid in its reaction with NR at mixing temperatures

(100-140°C) be subject to as low degree as possible to negative catalysis or to side reactions with non-rubbers inevitably present in NR, and be easily and economically introduced on to the end of the poly(styrene) chain. Arguments that the group should be an 'ene' reagent and, of the several possibilities of these, an azodicarboxylate were detailed in the First Progress Report (2.4.1). Subsequent examination of other examples, sulphonyl isocyanates and sulphonyl imines (Fourth Progress Report 2.4.5) have not altered this choice.

Initially the route devised to azopoly(styrene) involved several chemical stages with, in some, a change of solvent to suit reaction condition or solubility requirements.



Although this multi-stage sequence could not be regarded as economically or experimentally feasible for possible industrial scale application it was very encouraging that final azo functionalities averaging 70 per cent and as high as 81 per cent were obtained in the first series of experiments (Table 1, 2.4.2, Appendix, First Progress Report) indicating that each step was well over 90 per cent efficient.

The product was a pale yellow powder which did not lose functionality on storage for many months at ambient temperature in indirect daylight (see Table 1) or for up to 8 hours at 140°C indicating that decomposition under normal mixing conditions will be negligible. At 180°C decomposition was complete in 5 hours suggesting that high temperature processing should be avoided. (Third Progress Report, 2.1.4).

TABLE 1 STORAGE STABILITY OF AZOPOLY(STYRENE)

Initial azo functionality *	86
Azo functionality after 11 months	87

*from UV absorbance in methylene dichloride
(λ max 407 nm; ε = 34)

2.2.3 Grafting of azo-poly(styrene) to NR

It was readily demonstrated, as expected, that grafting of azo-capped poly(styrene) occurred efficiently, indeed quantitatively, to pure poly(isoprene) hydrocarbon when the two components were mixed in cyclohexane solution at 60°C.

TABLE 2 SOLUTION GRAFTING OF AZOPOLY(STYRENE) TO IR AND NR

	Azo-poly(styrene)		Poly(Isoprene)	Grafting
M_n	Functionality (%)	Wt%		Efficiency(%)
8 900	77	40	IR[1]	77
"	"	"	NR[2]	57
"	"	"	NR[3]	79

[1] Cariflex IR 305

[2] SMR 5L

[3] Extracted SMR 5L

From the point of view of potential commercial exploitation in NR, the solution reaction is of no immediate relevance. The expense of preparing a suitable solution of the NR would make the overall operation very costly and could only be justified if the final product could be sold at a very high premium. The poly(styrene) graft copolymers of NR, although possessing potentially useful properties, lie in a class of materials where price competitiveness is essential. For this reason, graft formation during direct mixing of the constituent polymers is the area of primary importance.

Fortunately, and perhaps surprisingly, grafting under such dry mixing conditions occurred almost as efficiently as in solution.

Small scale preparations of the graft copolymers were carried out in a Hampden-Shawbury Torque Rheometer. The machine consists of two contra-rotating paddles within a figure-of-eight cavity. The drive to the paddles is fitted with a torque transducer which provides a continuous record of mixing torque. A thermocouple in the cavity wall provides a measure of the mixing temperature and the cavity can be heated by oil circulation from an external heater. The mixing speed is continuously variable from 0 to 150 rpm giving a range of shear conditions up to that required for good dispersion of reinforcing carbon black. Chopped rubber and poly(styrene) powder were fed to the mixer as rapidly as possible at zero time at the appropriate machine settings and mixing was carried out continuously for the required time (usually 10 min).

Samples of the graft copolymers were compression moulded at 150°C into 0.5 mm thick sheets and test samples were cut from the sheets with appropriate dies.

Figure 1 compares the mixing torque as a function of mixing time for two mixes of poly(styrene) with synthetic cis-poly(isoprene) (Cariflex IR 305). The poly(styrene) samples have similar molecular weights but one sample has azo-dicarboxylate functionality and the other does not. With unreactive poly(styrene) the torque decreases more or less continually with mixing time as the rubber undergoes mastication. The final product is opaque and very weak at room temperature. With the functional poly(styrene) there is a pronounced maximum in the torque trace centred around a mixing time of six minutes. The final product is almost transparent and is very tough at room temperature.

The large peak in the torque trace represents the grafting reaction. This is confirmed by the results in Figure 2 which shows the measured grafting efficiency (by gpc analysis) at different mixing times along the torque trace.

The shape of the torque curve is dependent on both the mixing speed and on the initial cavity temperature. In general, higher mixing speeds and higher initial temperatures lead to faster reaction but if the initial temperature is too high the shear forces are reduced and the reaction becomes less efficient. There is, of course, a complex relationship between mixing speed, initial cavity temperature, composition of the mix and the final temperature of the mix because of the generation of work heat in the system. This relationship has not been completely evaluated.

For mixes with NR (SMR 5L) the same general behaviour is observed but the temperature of the mix is generally slightly higher at a given mixing speed and cavity temperature setting.

From these results a standard mixing condition of 10 min at 150 rpm at an initial cavity temperature setting of 90°C was selected for the preparation of materials for testing. These conditions ensured that the grafting reaction had gone to completion for all mixes.

2.2.3.1 Grafting efficiency The proportion of styrene grafted to the backbone chain is determined directly by the ratio of the two constituents which are fed to the mixing process. Ideally all the poly-(styrene) prepolymer which is added would be combined and the graft composition would be identical to the feed composition. In practice the poly(styrene) prepolymer has less than 100 per cent functionality because of imperfections in the synthetic sequence. Also, non-rubber constituents, particularly in NR, can interfere with the reaction of the pre-polymer with the backbone. These two factors combine to give some ungrafted poly(styrene) in the final product. The ratio of grafted to ungrafted poly(styrene) is best determined by gel permeation chromatography (gpc) which in most instances will resolve the high molecular weight graft polymer and the low molecular weight ungrafted poly(styrene). An example of a chromatogram is shown in Figure 3 together with a chromatogram of the original poly(styrene) prepolymer run under the same conditions. Component detection is by uv absorption at 262 nm, giving response only from the poly(styrene) constituents, ie there is no significant response from the poly(diene) backbone. The areas of free poly(styrene) and grafted poly(styrene) peaks can be used to calculate a grafting efficiency which is defined as the percentage of the poly(styrene) feed which becomes bound to the backbone.

The grafting efficiency under the standard mixing conditions is essentially independent of the amount of poly(styrene) in the feed when the backbone polymer is Cariflex IR 305 cis-poly(isoprene), indicating that there is no interference from non-rubber constituents in the backbone polymer. With NR (SMR 5L) there is a progressive decrease in grafting efficiency as the amount of poly(styrene) is decreased relative to NR, due to some wastage of azodicarboxylate groups by reaction with non-rubbers. This can be overcome by extracting out the interfering impurities with acetone but this is obviously not a commercially viable solution. Results for one particular batch of azodicarboxylate terminated poly(styrene) are given in Table 3.

TABLE 3 DRY MIX GRAFTING OF AZOPOLY(STYRENE) TO IR AND NR

	Azo-poly(styrene)		Poly(Isoprene)	Grafting
$\bar{M}_n$	Functionality (%)	Wt%		Efficiency(%)
8 900	77	40	IR[1]	74
"	"	20	IR[1]	76
"	"	40	NR[2]	45
"	"	20	NR[2]	26
"	"	40	NR[3]	73

[1] Cariflex IR 305

[2] SMR 5L

[3] SMR 5L after acetone extraction

2.2.4 Physical properties of poly(styrene) - NR grafts

The graft products from direct mixing of azodicarboxylate terminated poly(styrene) with NR under appropriate conditions are rubbers of varying modulus and strength depending on their composition and they are thermoplastic, ie they can be moulded directly at elevated temperatures to give samples with the full range of physical properties without any need for a vulcanization sequence. In general terms, they are comparable to block copolymers of styrene and diene but because of the very fundamental difference in molecular architecture compared with the block copolymers, many differences in detailed behaviour must be anticipated.

There are two primary mechanisms for controlling the physical properties of the graft copolymers. The first is control of the proportion of styrene graft to diene backbone and the second is control of the molecular weight of the poly(styrene) graft chains. A third variable, the molecular weight of the poly(diene) backbone is not directly controllable since it is affected by mastication during the grafting process.

The molecular weight of the poly(styrene) grafted chains is determined at the synthesis stage of the poly(styrene). Figure 3 confirms that there is no mechanical degradation of the free poly(styrene) during the mixing operation (identical retention times for the free poly(styrene) and the original poly(styrene) prepolymer) and it is assumed that the grafted poly(styrene) chains are also unaffected. The assumption is a reasonable one since the molecular weight of the poly(styrene) is very much less than that of the backbone polymer and the mixing stresses will be carried preferentially by the backbone polymer. Changing the poly(styrene) molecular weight at a fixed feed composition does not affect the final composition of the graft copolymer but it alters the structure. The higher the poly(styrene) molecular weight the fewer the number of graft chains there will be for a fixed composition and the higher will be the molecular weight of the backbone segments between the graft sites.

2.2.4.1 Effect of poly(styrene) content on physical properties

Increasing the poly(styrene) content of the graft copolymer gives progressively harder products. A range of materials from very soft rubbers to impact resistant plastics can be formed and the 'optimum' properties can be defined only in the context of end product use. The azodicarboxylate terminated poly(styrene) required to operate the process is likely to be considerably more expensive than the poly(isoprene). There was therefore little point in devoting effort to the study of materials with high poly(styrene) contents which will probably have properties very similar to those of conventional high-impact poly(styrene).

Attention has therefore been confined to the more rubbery products. For a preliminary evaluation of the materials conventional rubber tensile testing was used.

The ultimate tensile strength of the graft copolymers is shown as a function of poly(styrene) content in Figure 4. There are two significant features of these results. The first is that there is a maximum in tensile strength at 40 to 45 per cent poly(styrene), the strength decreasing as the material begins to show plastic failure at the high poly(styrene) contents. The second feature is that the NR graft copolymers show consistently higher strength at a given total poly(styrene) content than those derived from synthetic poly(isoprene) in spite of the fact that the grafting efficiency with NR is lower. The higher strength of the NR products arises from higher modulus at high elongations rather than from increased elongation at break and is almost certainly due to the ability of NR to crystallise under stress.

2.2.4.2 <u>Effect of poly(styrene) molecular weight</u> Figure 5 shows the effect of the poly(styrene) molecular weight on the tensile strength of the graft copolymers at constant overall poly(styrene) content (40 per cent w/w). There is a very pronounced maximum at a poly(styrene) $\bar{M}_n$ of [illegible]0 to 8 000 for both the synthetic poly(isoprene) and the NR based m[illegible]s. The same behaviour is observed at other poly(styrene) contents and similar but less pronounced trends occur in the modulus at different extensions.

For the NR graft copolymers the grafting efficiency decreases as the poly(styrene) molecular weight increases, due to an increased proportion of azodicarboxylate end groups being consumed by non-rubbers but with Cariflex IR 305 there is no analogous fall-off of grafting efficiency. The decrease in modulus and tensile strength with increasing poly(styrene) molecular weight is therefore a direct physical effect of the poly(styrene) molecular weight or of the necessary change in graft site frequency as the molecular weight is changed at a constant poly(styrene) level.

A full explanation of the dependence of strength on poly(styrene) molecular weight cannot be offered at present. The effect is almost certainly related to the detailed morphology of the graft copolymers and represents an area where the graft copolymers differ in a very basic way from styrene-diene block copolymers.

2.2.4.3 *Comparison with commercial block copolymers* Samples of two commercial block copolymers (Kraton 1101, SBS; Kraton 1107, SIS) were compression moulded under the same conditions as the graft copolymers and the tensile properties were measured. The results are shown in Table 4. The moduli are lower than for graft copolymers of the same poly(styrene) content and the tensile strengths are considerably higher. The high tensile strengths are a consequence of much higher elongations at break compared with the graft copolymers. However, these commercial grades of block copolymers are not used directly for manufacturing purposes. They are compounded with oils and resins before use and they are designed specifically for adhesives applications. Similar compounding is carried out on all grades intended for moulding applications.

TABLE 4 TENSILE PROPERTIES OF KRATON 1101 AND KRATON 1107 BLOCK COPOLYMERS

	Kraton 1101	Kraton 1107
Poly(styrene) content (% w/w)	32	10
M100 (MPa)	2.18	0.58
M300 (MPa)	2.84	0.84
M500 (MPa)	5.12	1.14
M700 (MPa)	13.5	1.67
Tensile Strength (MPa)	32.2	12.5
Elongation at break (%)	857	1149

Published information for Kraton injection moulding compounds based on SBS block copolymers show that tensile strengths range from 3.8 to 20 MPa with no fewer than four grades having tensile strengths lower than [illegible] MPa. Similar information on Phillips Solprene thermoplastic rubbers shows a range of tensile strengths from 5 to 11 MPa. Measurements in our own laboratory on a range of commercial compounds gave tensile strengths from 4 to 8 MPa.

The graft copolymers, particularly those from NR, can show sufficiently high tensile strengths to allow the possibility of compounding with other (cheapening) ingredients and still provide moulding compounds of comparable strength to commercial products.

2.2.5 Improvement of the capping chemistry

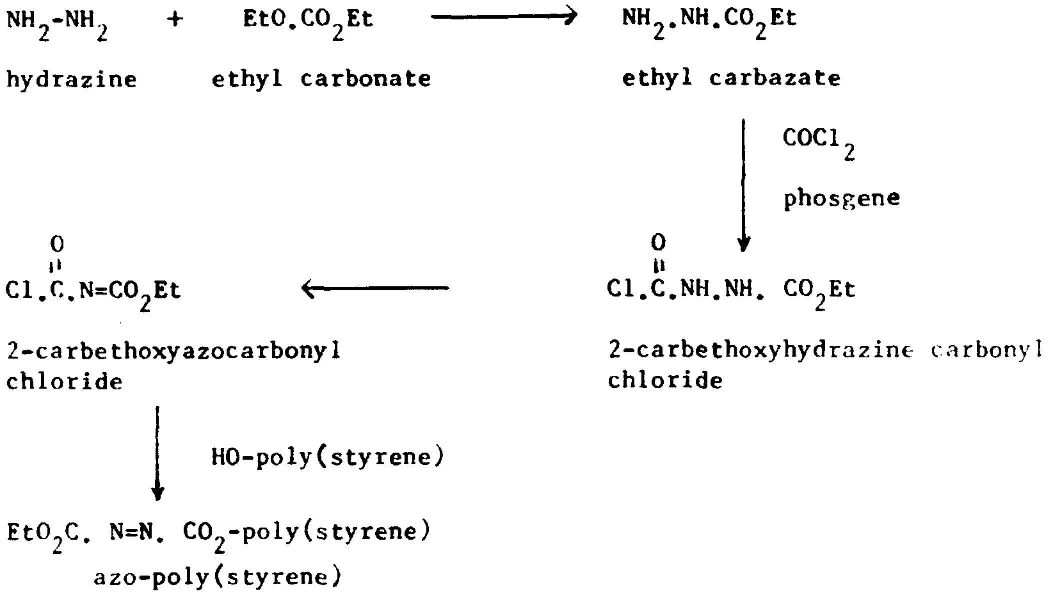
The route to azo-poly(styrene) detailed already in 2.2.1 was adequate to allow the grafting concept to be established but had serious deficiencies so far as a viable commercial process was concerned. Four consecutive steps manipulating a polymer end group were involved. Had each of these been 90 per cent efficient in terms of end group yield the final azo functionality would be only 65 per cent of theory. In addition the reaction sequence involved handling the polymer in three different solvents (cyclohexane, tetrahydrofuran and dichloromethane) with precipitation and drying of the polymer at each change of solvent and at the end of the sequence.

Such a procedure could not be translated to the large scale and no attempt was made to cost it. Instead, efforts were concentrated on its simplification.

2.2.5.1 Azo acid chloride concept

The minimum azo functionality requirement was set at 65 per cent although the highest level possible is obviously desirable. As shown above, a four-stage process has to have a very high efficiency at each stage to achieve even 65 per cent efficiency overall. Therefore for manipulative, economic and efficiency considerations a reduction in the number of stages is clearly indicated.

The concept devised was to synthesise by straightforward organic chemical steps an azodicarboxylate functionalised with an acyl chloride group. This was then to be linked directly to hydroxypoly(styrene) to give the azo polymer in one polymer handling stage other than the initial polymerization.



$NH_2\text{-}NH_2 + EtO.CO_2Et \longrightarrow NH_2.NH.CO_2Et$

hydrazine, ethyl carbonate, ethyl carbazate

$\xrightarrow{COCl_2 \text{ phosgene}} Cl.\overset{O}{\overset{\|}{C}}.NH.NH.\ CO_2Et$

2-carbethoxyhydrazine carbonyl chloride

$\longrightarrow Cl.\overset{O}{\overset{\|}{C}}.N{=}CO_2Et$

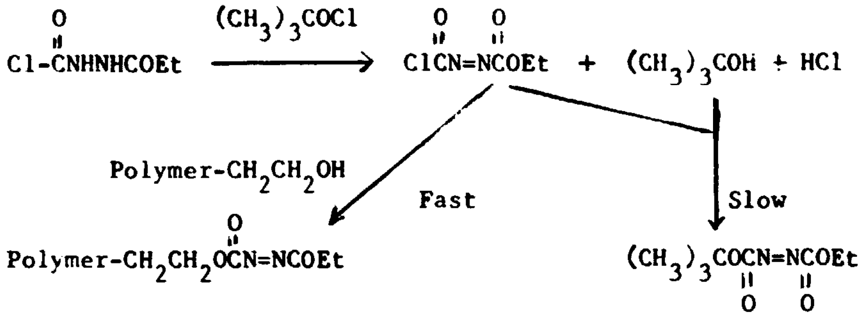
2-carbethoxyazocarbonyl chloride

$\xrightarrow{\text{HO-poly(styrene)}} EtO_2C.\ N{=}N.\ CO_2\text{-poly(styrene)}$

azo-poly(styrene)

The crucial steps in this sequence are the final two - the oxidation of the hydrazine to azo and the condensation of the azo acid chloride with the hydroxy polymer. A full discussion of the oxidants available for the hydrazine and the analysis, stability and condensation of the azo acid chloride is to be found in the Second Progress Report (Section 2.3), the Third Progress Report (2.4) and the Fourth Progress Report (2.4).

Initially the oxidant chosen was bromine/pyridine but the presence of pyridine was found to be detrimental to the efficiency of capping and also to the subsequent grafting reaction of the azo polymer. Moreover, pyridine is expensive. A significant step forward was made by the introduction of t-butyl hypochlorite as the oxidant (Third Progress Report, 2.4.1, 2.4.2). t-Butyl hypochlorite may be regarded as a stabilised form of hypochlorous acid and has been used to obtain azo compounds. The other products are hydrogen chloride and t-butanol. It was anticipated that t-butanol could react with the oxidation product, carbethoxyazocarbonyl chloride. This reaction with a tertiary alcohol should be slower than the reaction with a terminal primary hydroxyl group on poly(styrene). The new approach is shown in the scheme below.



Pyridine is no longer an integral part of the oxidation sequence. Total omission of pyridine from the system is expected to result in a slower reaction with the alcohols present, giving potentially greater selectivity for reaction with the primary rather than tertiary hydroxyl group. This selectivity is highly critical. The tipping agent must be performed in dichloromethane solution (owing to the insolubility of 2-carbethoxyhydrazinecarbonyl chloride in hydrocarbon solvents) and subsequently added to the poly(styrene) which is currently prepared as a solution in toluene. t-Butanol will be formed as a by-product during the initial oxidation, prior to addition to the poly(styrene) and the reaction of t-butanol with tipping agent must be sufficiently slow to prevent significant losses of tipping agent during its preparation.

t-Butyl hypochlorite is very readily obtained by the oxidation of t-butanol using sodium hypochlorite solution acidified with acetic acid. Satisfactory material could also be obtained by chlorination using chlorine under basic conditions but this method is much less convenient. 2-Carbethoxyhydrazinecarbonyl chloride was dissolved in dichloromethane, stirred and cooled in an ice bath in the dark. Stirring with excess t-butyl hypochlorite gave a yellow solution of tipping agent after 10-20 min. If the solution is used immediately, it will effect satisfactory tipping of solutions of hydroxy poly(styrene) in toluene, as obtained in the current method of preparation. Reaction with the poly(styrene), say $\bar{M}_n$ 7 500, as a 20 per cent solution in toluene using 50-100 per cent excess reagent was complete in 4 hours, and no significant increase in tipping was noted when a further 12 hours reaction time was allowed. Isolation using precipitation into methylated spirits and drying presented no problems on this scale. Tipping efficiencies as measured by gpc analysis of torque rheometer mixes are now typically >80 per cent, Table 5.

TABLE 5 MOLECULAR WEIGHTS, FUNCTIONALITIES AND GRAFTING EFFICIENCIES OF AZODICARBOXYLATE TERMINATED POLY(STYRENE) PREPARED WITH 2-CARBETHOXYHYDRAZINECARBONYL CHLORIDE OXIDISED EXTERNALLY WITH t-BUTYL HYPOCHLORITE

Polymer	Calculated $\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Silicon $\bar{M}_n$	Azo[a] $\bar{M}_n$	Functionality[b] (%)	Grafting[c] Efficiency
SP24	7 489	7 615*	1.04	9 330	9 066	84.0	82.6
SP31	5 332	5 590†	1.06	6 560	6 273	89.1	85.0

* $\bar{M}_n$ by gpc † $\bar{M}_n$ by vpo

[a] Calculated from the absorbance at 407 nm using 34 as the extinction coefficient for azodicarboxylate

[b] Calculated from azo $\bar{M}_n$ and measured $\bar{M}_n$

[c] Measured for grafting to Cariflex IR 305 in the Torque Rheometer. Mixing time 10 min.

2.2.5.2 Raw material costs of process

It can be assumed that the final material produced by the process, ie the product of mixing the capped poly(styrene) with NR, will need to be price-competitive with SBS/SIS-type synthetic thermoplastic rubbers. It is tacitly assumed that the cost of mixing the poly(styrene) with NR can be disregarded. That is to say, the target is to produce a poly(styrene) at a price which, when mixed with the appropriate quantity of NR, equates with that of the synthetic thermoplastics.

The West European price for the SBS material is around £900/tonne; that for SIS is £1 100 (Shell). These are prices for the raw polymer; more often, these materials are sold as ready-to-use compounds. Assuming therefore that the mixed NR/poly(styrene) must cost not more than about £1 000/tonne, and given that (i) the mix typically contains 35 per cent poly(styrene), and (ii) the price of NR is £600/tonne, then the poly(styrene) price which a consumer would regard as equivalent to that of SBS/SIS synthetics is £1 700/tonne. Variations in the price of NR are to some extent dampened by the mix composition: an NR price of £800/tonne produces a mix cost of just over £1 100/tonne.

It is not possible at this stage to assess the total processing costs for preparing the capped poly(styrene) on a commercial scale. It will be arbitrarily assumed that the raw materials cost for the poly(styrene) should not exceed about one-third of the price of the finished poly(styrene) (£1 700/tonne) in order to give adequate leeway for operating and financial costs. Thus, a total raw materials cost in the vicinity of £600/tonne can be taken as a target.

The annexed scheme sets out the process as initially operated on a laboratory scale. The quantities on the chart are for the 1 mole scale to produce a capped poly(styrene) of molecular weight 7 500. Two reaction sequences are involved: (i) preparation of anionically-polymerized poly(styrene) terminated with hydroxyl groups, and (ii) preparation of the chlorinated azo ester. Reaction between the two produces the capped azopoly(styrene).

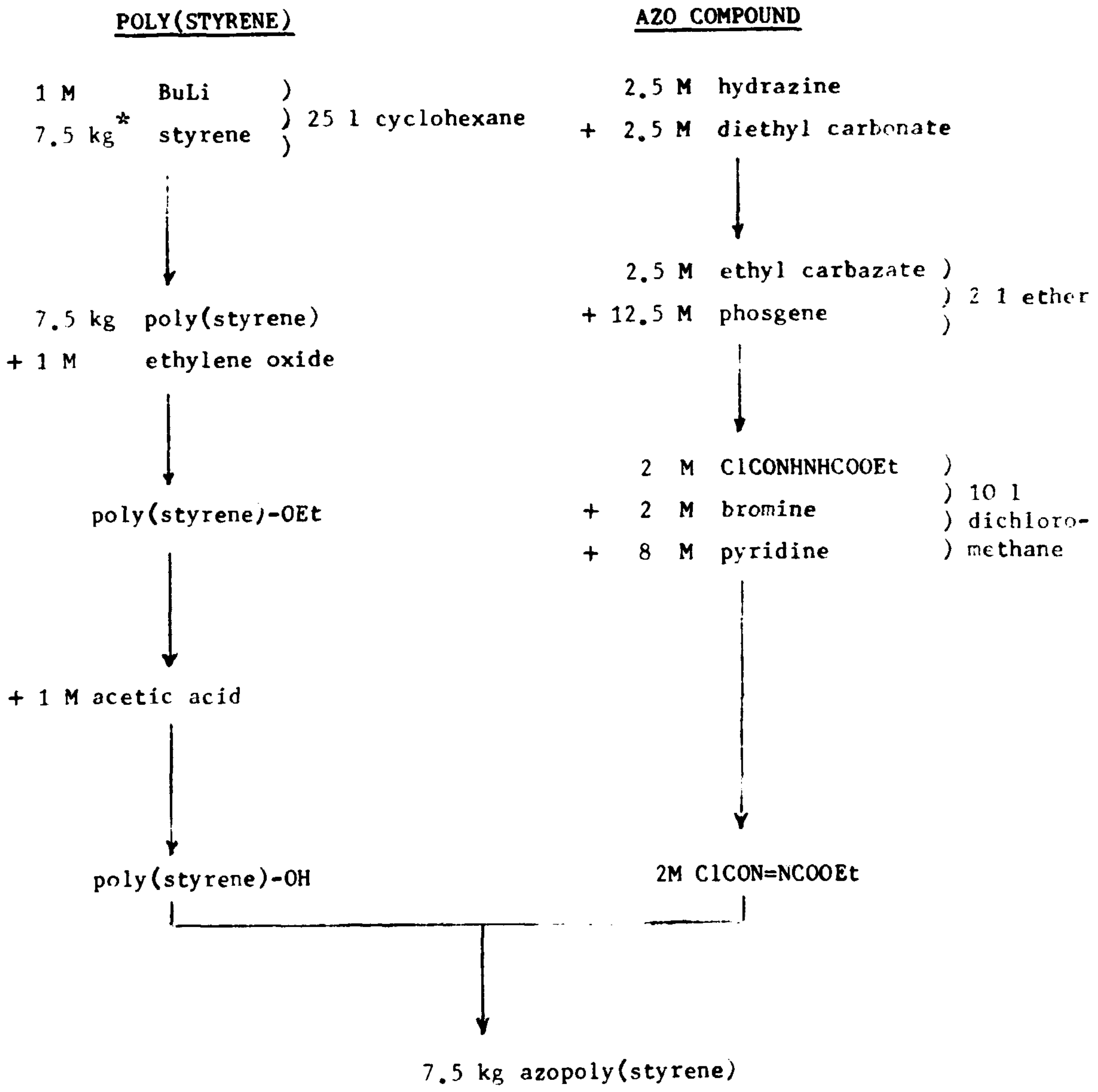
The process illustrated uses substantial excesses of certain reagents; this applies especially to phosgene, a very expensive chemical. It will also be noted that the final reaction involves 2 moles of azo acid chloride to 1 of poly(styrene).

In theory some of the reactants will be combined with the poly(styrene) and will therefore add to the weight of polymer produced. In practice, recovery of polymer is not 100 per cent and experience so far suggests that it is adequate to assume 100 per cent recovery of polymer without addition to its weight of other groups.

In the subsequent cost analyses no account is taken of the precipitant used to isolate the poly(styrene), since on a commercial scale precipitation is most unlikely to be used.

The method of arriving at raw materials costs was given in the Second Progress Report (Section 2.4.4) and the results are given in Table 6.

SCHEME CHEMICALS REQUIRED FOR PRODUCTION OF AZOPOLY(STYRENE)



* for $\bar{M}_n$ 7 500

TABLE 6 QUANTITIES AND COSTS FOR AZOPOLY(STYRENE) PROCESS

	Quantity	g	Price £/tonne	£/tonne of poly(styrene)
cyclohexane	25 l	19 450	200	519
dichloromethane	10 l	13 270	330	584
ether	2 l	1 428	800	152
n-BuLi	1 M	64	12 500	107
ethylene oxide	1 M	44	385	2
acetic acid	1 M	60	215	2
hydrazine	2.5 M	125	2 000	33
diethyl carbonate	2.5 M	295	1 200	47
phosgene	12.5 M	225	3 000	490
bromine	2 M	320	400	17
pyridine	8 M	632	2 000	168
				2 121
styrene		7 500[1]	325	325
				2 446

[1] for a poly(styrene) of molecular weight 7 500

The total cost arrived at in Table 6 is greatly in excess of the target figure and served to concentrate effort on cost reduction. It is, however, unrealistic insofar as it makes no allowance for solvent recovery. Economic and environmental requirements will necessitate some recovery but it is hard to say what recovery level is feasible until the final choice of solvent has been made, and this choice may need in part to be determined by the need to achieve efficient recovery. One would aim to recover at least 90 per cent, and Table 7 shows the effect of this on cost.

TABLE 7 **EFFECT OF SOLVENT RECOVERY**

Recovery (%)	Total cost, £/tonne
0	2446
50	1818
90	1316

The most obvious approach to further cost reduction was the elimination of the need to use reagents in excess. This is especially important in the case of phosgene. Table 8 shows the effect on costs of achieving complete stoichiometry in all stages.

TABLE 8 **EFFECT OF ACHIEVING FULL STOICHIOMETRY**

	£/tonne poly(styrene)		
	present	full stoichiometry	cost reduction
solvents*) styrene) initiator)	557	557	
ethylene oxide	2	2	
acetic acid	2	2	
hydrazine	33	13	20
diethyl carbonate	47	19	28
phosgene	490	39	451
bromine	17	8	9
pyridine	168	63	105
	1316	703	613

* 90% recovery

Evidently, attention to stoichiometric aspects could achieve substantial cost savings; the reduced total cost approaches the £600/tonne target.

Cost reduction could also be achieved by increasing the poly(styrene) molecular weight: one is attaching an expensive end group to a relatively cheap polymer and the longer the polymer chain the lower the total cost per unit weight. The effect is not linear and there is a progressive reduction in benefit as the molecular weight is increased. Table 9 shows the effect in the case of the 'full stoichiometry' model of Table 8 although it must be emphasised that for property requirements it may not be possible to depart from the 5-10 000 region for the molecular weight of poly(styrene).

TABLE 9 EFFECT OF POLY(STYRENE) MOLECULAR WEIGHT

Molecular weight	Cost £/tonne	Change in cost/tonne (£) per 1000 units increase in molecular weight
5 000	892	-113
7 500	703	- 50
10 000	608	- 23
15 000	514	- 13

As indicated earlier (2.2.5.1) it proved both possible and chemically desirable to replace bromine/pyridine as the oxidant for the hydrazocarbonyl chloride by a less expensive reagent, t-butyl hypochlorite. Attention was also paid to minimising the excess of reagents used, eg phosgene (Second Progress Report, 2.3.3) with the result that the list of solvents/reagents has now been modified as in Table 10 with a consequent further reduction in costs.

The final figure of £677/tonne has to be compared with the £703 obtained for a hypothetical 'full stoichiometry' situation in Table 8 remembering that the latter was based on the use of bromine/pyridine as oxidant.

It is now considered that the scope for reducing costs further by improvements to the chemistry or stoichiometry is slight. Very recent work suggests that the 50 per cent excess of 2-carbethoxyazocarbonyl chloride now used in final capping stage can be reduced without loss of efficiency. This would result in a saving of ca £40/tonne (the excess of oxidant used to produce the azocarbonyl chloride must be maintained).

Additional savings of £50/tonne could be made by a slight increase in the poly(styrene) molecular weight as detailed in Table 9.

TABLE 10 SUMMARY OF COST REDUCTIONS FOR AZOPOLY(STYRENE) PROCESS

Reagents/solvents	Quantity		£/tonne of poly(styrene)	
	formerly	now	formerly	now
cyclohexane	25 l	20 l	519	415
dichloromethane	10 l	1.5 l	684	88
ether	2 l	2 l	152	152
n-BuLi	1 M	1 M	107	107
ethylene oxide	1 M	1 M	2	2
acetic acid	1 M	1 M	2	2
hydrazine	2.5 M	1.5 M	33	20
diethyl carbonate	2.5 M	1.5 M	47	28
phosgene	12.5 M	2 M	490	78
bromine	2 M		17	
pyridine	8 M		168	
t-Bu hypochlorite		1.5 M		50
			2 121	942
styrene	7 500 g		325	325
			2 446	1 267
With 90% solvent recovery			1 316	677

It can be concluded, therefore, that the capping chemistry has been improved to the point where the raw materials cost of the azopoly(styrene) will be very close to or under the target figure of £600/tonne.

2.2.6 Scaling up of the production of azo-capped poly(styrene)

The initial laboratory scale polymerization of styrene was adequate to support the investigational work on the capping chemistry and the dry mix grafting in the Torque Rheometer. The translation to grafting in the BR Banbury mixer required a batch size of 1.5 kg of mix or ca 450 g of azopoly(styrene). Thus the whole of a preparation taking several days would be consumed in a few minutes.

The primary requirement for improving the supply of azopoly(styrene) is increased availability of the hydroxyl terminated polymer. An external source of hydroxyl terminated poly(styrene) would have been of considerable assistance and some effort was made to find such a source in the United Kingdom. Two groups were located which were carrying out anionic polymerization of styrene on a 1 kg scale, but only one of the groups had experience of termination of the polymer with oxirane to give hydroxyl functionality. At one time they contemplated a scaling-up operation to a flow reactor system but it now seems improbable that they will proceed with the project.

A 16.5 l metal batch reactor was designed and built (see Figure 6) to accommodate the polymerization of up to 2 kg of styrene. At maximum output this could enable up to this weight of azo-polymer to be synthesized per day and is probably the largest batch unit that could be contemplated because of the problem of heat dissipation.

It should, nowever, be noted that the polymerization is well suited to a flow reactor system and any further development of the synthesis should be considered in this context. The batch reactor is based on a stainless steel portable autoclave (Griffin catalogue No.S12-922) of internal diameter 270 mm and internal height 290 mm. The total volume is 16.5 l. The rubber sealing ring for the lid is replaced by a PTFE coated cork gasket. Internal cooling is provided by a coil (180 mm diameter x 180 mm high) of stainless steel tubing. The tubing is 6.36 mm OD and 4.62 ID and the total length is 4.05 m. The coil is attached to the lid of the reactor by Hoke Gyrolock bulkhead fittings and thence to the bench cold water supply via plasticised PVC tubing. A glass condenser (Sovirel Laboratory Glassware, catalogue No.4.774.22; 250 mm working length) is fitted to the lid of the reactor via a stainless steel adapter. Agitation is provided by a stainless steel paddle stirrer fitted via a purpose-made stainless steel/PTFE stirrer gland. Monomer, solvent and initiator solution are charged to the reactor via the same 6.36 mm OD stainless steel tube fitted to the lid of the reactor through a Hoke Gyrolock bulkhead fitting. The discharge is via a similar tube entering the side of the reactor 140 mm from the bottom and dropping to within 2 mm of the bottom internal surface. The discharge tube also serves as an inlet for purge gas and for ethylene oxide. A stainless steel thermocouple well extends from the reactor lid to within 100 mm of the bottom of the reactor. The reactor is mounted on Dexion framework with the bottom half completely unobstructed and raised 200 mm above the bench surface. This allows the use of external heating or cooling baths if necessary.

Solvent and reagents are supplied to the reactor via 6.36 OD tubing (stainless steel or PTFE) assembled with Hoke Gyrolock fittings and valves. Liquid transfers are through stainless steel except where some flexibility is necessary. Gas pressure for liquid transfer is directed through PTFE tubing. The pipework arrangement is shown schematically in Figure 6. Glass measuring vessels (A, B, C; Figure 6) are incorporated for metering the addition of solvent/monomer, initiator and ethylene oxide respectively. Redistilled solvent is stored in a 25 l drum and redistilled monomer in a 2.5 l brown glass vessel, both of which are attached to the pipework system of the reactor. The supplier's bottles of initiator solution can be attached directly to the pipework system via a purpose-made adapter without exposure to the atmosphere. Ethylene oxide is stored in the supplier's cylinder and is dried over calcium hydride in vessel C immediately before use.

The reactor vents through the reflux condenser and 15 mm OD copper tube to a 22.5 l steel can. The can subsequently vents to the atmosphere through a mercury trap having a forward venting pressure of approximately 20 mm Hg above atmospheric pressure and a resistance to suckback of approximately 300 mm Hg below atmospheric pressure. The wide bore venting to an enclosed can acts as a safety measure to allow mechanical carry-over of reactor contents if overheating and rapid boiling takes place in the reactor.

The reactor is operated in an atmosphere of dry nitrogen. The gas supply is fed through a column of 5A molecular sieve 1.5 m long by 30 mm diameter.

2.2.6.1 Typical preparation of azopoly(styrene) on a 1.5 kg scale

Toluene was dried by azeotropic distillation and distilled under nitrogen. Styrene monomer was stirred over calcium hydride overnight and distilled from fresh calcium hydride under reduced pressure. Antioxidant 425 (10 ppm) was added to the monomer after distillation. Initiator solution was used as received (sec-butyl lithium, nominally 1.3M).

The reactor was kept under positive nitrogen pressure for two days after the previous polymerization. The reactor was charged with toluene (250 ml) and a small amount of styrene monomer and n-butyl lithium solution (20 ml, 1.6M) was injected from a syringe into a port in the reactor lid. Sampling of the purge solution at intervals via the discharge tube showed that the dark red colour was retained after 30 min. The purge solution was discharged and the reactor was rinsed with toluene (2 x 250 ml).

Styrene monomer (1 650 ml) and toluene (3 875 ml) were charged to the reactor and the cooling water was turned on full to the condenser and the cooling coil. The temperature of the monomer solution stabilised at 7.5°C. sec-Butyl lithium solution (1.3M, 190 ml) was charged to the reactor in two batches over 45 sec and the reaction temperature was recorded as a function of reaction time. At 13 min reaction the temperature levelled off at 25.5°C. Water to the cooling coil was turned off at 15 min reaction and the temperature was allowed to rise for 5 min. The cooling water was then turned on again, bringing the temperature immediately under control.

Ethylene oxide was stirred over calcium hydride for 1.5 hr during the setting up of the polymerization and the required volume (15 ml) was transferred to the reactor 45 min after the start of the polymerization. The cooling water had been turned off and the polymer solution was at 28.5°C. After the ethylene oxide addition, the solution temperature rose to 35°C. After 1 hour the polymer solution was discharged into a 10 l aspirator containing glacial acetic acid (17.5 ml). The aspirator was fitted with a mechanical stirrer.

While the polymer was being transferred to the aspirator, 2-carbethoxyhydrazinecarbonyl chloride (62 g, 0.371 mole, approximately 50 per cent molar excess over polymer end groups) was weighed into a dry 1 l 3-neck flask in a dry box. Dry dichloromethane (400 ml) was added and the closed flask was set in an ice bath. t-Butyl hypochlorite (42 ml, 40 g, 0.381 mole) was added from a pressure equalised funnel over 5 min and the reaction mixture was stirred until all solid hydrazo acid chloride had dissolved. The deep orange red solution was transferred to the acidified polymer solution through a tube, using nitrogen pressure.

The polymer solution was stirred at room temperature overnight then washed with water (3 x 5 l). Each batch of water was stirred rapidly with the polymer solution for 10 min and the mixture was allowed to settle to a clear aqueous lower layer (approximately 90 per cent of the added water) and an emulsion of water in the polymer solution. After the final washing, the emulsion was clarified by stirring with methylated spirits (2 l) to give a lower layer of polymer solution which was removed from the aspirator and sprayed into methylated spirits (20 l) using a paint spray gun. The polymer was collected by filtration and dried in vacuo at 35°C. It had an estimated azo functionality of 86 per cent and a grafting efficiency with Cariflex IR 305 of 80 per cent.

Information on the reaction conditions and results of the initial series of polymerizations carried out in the reactor are given in Table 11.

All the preparations were carried out in toluene solution using sec-butyl lithium as initiator. The reaction scale varied from 0.7 to 2 kg of polymer at initial monomer concentrations ranging from 21 to 40 per cent by volume. Three different batches of initiator solution were used, one of which was nominally 7 per cent more concentrated than the other two. No attempt was made to check the initiator concentration independently and the theoretical number average molecular weights ($\overline{M}_n$) were calculated from the nominal initiator concentrations. The observed values of $\overline{M}_n$ were always higher than the calculated values. In general, the discrepancy was reasonably consistent within results for one batch of initiator with the exception of results for polymers RPS 11 and RPS 12. The initiator batch used for polymers RPS 9 and RPS 10 was stored for four weeks at room temperature attached to the apparatus before

TABLE 11 AZODICARBOXYLATE TERMINATED POLY(STYRENES)

Polymer	Monomer volume (ml)	Monomer conc. (% v/v)	Initiator volume (ml)	Max. reaction temp. (°C)	Calculated $\overline{M}_n$	GPC		'Dimer' in OH polymer (%)	Azo functionality (%)	Grafting efficiency (%)
						$\overline{M}_n$	d			
RPS 1	800	21	65[a]	34	7980	9830	1.07	11.5	75[e]	57
RPS 2	1150	30	94[a]	52	7980	9670	1.06	9.6	79.5[e]	61
RPS 3	1650	30	134[a]	45	7980	8689	1.05	5.8	78[e]	65
RPS 4	1650	30	134[a]	49	7980	9133	1.63	12	-	-
RPS 5	1650	30	135[a]	51	7980	9164	1.14	3	97[f]	88[fg]
RPS 6	1650	30	190[b]	50	6070	7100	1.10	>>1	94	78
RPS 7	2210	40	254[b]	-[d]	6070	6420	1.11	1	66	-
RPS 8	2210	30	254[b]	89	6070	6570	1.10	1	66	-
RPS 9	1650	30	190[c]	45	6070	6550	1.09	>>1	75	71
RPS 10	1650	30	190[c]	47	6070	6630	1.07	>>1	86	80
RPS 11	1650	30	190[c]	42	6070	9300	1.07	>>1	71	61
RPS 12	1650	30	190[c]	53	7640	11350	1.09	>>1	90	80

a. Initiator solution nominally 1.4 M.

b. Initiator solution nominally 1.3 M.

c. Initiator solution nominally 1.3 M.

d. Vigorous boiling.

e. Polymer samples precipitated only once; samples may have been contaminated with ethyl t-butyl azodicarboxylate.

f. Average result for five samples.

g. Reaction with Cariflex IR 305 in solution; other grafting efficiencies are for dry mixing.

preparation of polymers RPS 11 and RPS 12. The increase in observed $\overline{M}_n$ for the latter polymers is a consequence of initiator decomposition during the storage period.

Early batches of polymer from the reactor contained substantial amounts of a polymeric component having twice the molecular weight ($\overline{M}_n$) of the main product. This 'dimer' almost certainly arose from traces of carbon dioxide present as air contamination of the reactor atmosphere. With the exception of preparation RPS 4, which was the first preparation after a lay-off period, the level of dimer decreases progressively with increasing use of the reactor, indicating progressive improvement in the reactor atmosphere. The 'dimer' component is undetectable in current preparations.

Table 11 lists the maximum recorded temperature for each reaction merely to demonstrate the conditions under which the reaction becomes uncontrollable. Polymerizations RPS 7 and RPS 8 were run under conditions of maximum cooling (full water flow in the cooling coil and condenser throughout the reaction). RPS 7 reached boiling point in 4 min and there was transfer of polymerising solution into the vent can via the reflux condenser. RPS 8 did not boil, but reached its maximum temperature (89°C) in 7 min. As a result of these experiments, the safe working scale for the reactor has been set at 1.5 kg at a monomer concentration of 30 per cent by volume. This limit is specifically for polymerization in toluene solution using sec-butyl lithium catalyst. Change of solvent or catalyst will alter the thermal characteristics of the reaction. The other maximum temperatures recorded in Table 11 do not necessarily represent reaction under maximum cooling conditions. Some reactions on a 1.5 kg scale show an initial maximum temperature of 25 to 30°C at about 15 min reaction under maximum cooling conditions. For these reactions, continued cooling would result in rapid retardation of the reaction and in such circumstances the cooling water is stopped for a short period to allow the temperature to exceed 35 to 40°C and ensure rapid completion of the polymerization.

The final azo functionalities ranged from very high to just above the arbitrary limit of 65 per cent which has been set.

Details of many more polymerizations using both sec-butyl and n-butyl lithium as catalysts are given in the Fourth Progress Report (2.1.2). It will be noted that n-butyl lithium used without an activator gives a slower initiation rate and a wider molecular weight dispersion. The effect of this on the physical properties of the graft is not yet known.

As well as tackling the immediate problems of the scale of preparation of the poly(styrene), some thought has been given to the longer term economic aspects of the synthesis; in particular, the source of the solvent/styrene monomer combination used as feedstock and the initiator/activator combination. Styrene monomer is produced industrially by catalytic dehydrogenation of ethyl benzene. The crude dehydrogenation mixture contains about 40 per cent w/w styrene in unreacted ethyl benzene and the pure monomer is obtained by fractional distillation. Until recently, the fractionation operation accounted for a considerable proportion of the cost of the pure monomer. With the rapidly increased cost of petroleum raw materials the relative importance of the fractionation in the final monomer cost is decreasing but there could still be a 15 per cent cost advantage if the crude dehydrogenation mixture could be used as the source of styrene. The polymerization of pure styrene in pure ethyl benzene (or toluene, which is a comparable solvent in the context of the polymerization reaction) with sec-butyl lithium as initiator has been shown to give poly(styrene) of predictable molecular weight and narrow molecular weight distribution (1.05). Termination with ethylene oxide and acidification gives high hydroxyl functionality. With n-butyl lithium as initiator in toluene solution the reaction is somewhat slower and the molecular weight distribution is wider (1.3 to 1.4) but hydroxyl functionality remains high. The presence of compounds containing oxygen or nitrogen activates the n-butyl lithium initiated polymerization and reduces the molecular weight distribution but can cause loss of functionality eg in an extreme case, polymerization in the presence of one molar equivalent of diglyme gave no hydroxyl functionality at all.

Polymerization of styrene in a sample of crude ethyl benzene dehydrogenation mixture with sec-butyl lithium resulted in a highly exothermic reaction which was impossible to control by external cooling. Impurities in the feedstock were 'titrated out' by slow addition of initiator solution until a permanent red colour was present. Additional initiator was then added as rapidly as possible, the amount being dictated by the amount of styrene monomer in the system and the desired molecular weight of the polymer. The amount of initiator solution consumed in the titration step was approximately 30 per cent of the total amount used. The feedstock therefore contained substantial amounts of reactive impurities and the products of reaction of these impurities with initiator behaved as activators for the initiation and propagation steps, giving a vigorous polymerization. This conclusion is supported by the results of a polymerization of ethyl benzene dehydrogenation mixture initiated with n-butyl lithium. By analogy with results in pure toluene, n-butyl lithium should give a relatively slow polymerization but in the dehydrogenation mixture the polymerization was as vigorous as with sec-butyl lithium. Both initiators form the same propagating anion and the activating impurities enhance the propagation rate in both reactions.

The use of the dehydrogenation mixture is probably not suitable for batch reactions but could merit further investigation if flow reactors are used for large scale polymerizations.

2.2.7 Larger scale mixing and compounding studies

Although it had been clearly established that efficient grafting of azo-poly(styrene) on to NR occurred during dry mixing in the torque rheometer it was obviously necessary to work on a larger scale using a more conventional mixer to show that grafting still took place without difficulty and to obtain sufficient material for compounding and property studies.

2.2.7.1 Mixing It was found possible to scale up the dry mixing process forty-fold by using a Farrel Bridge BR Banbury Mixer with a total charge of 1-1.5 kg. Limitations in the supply of azo-poly(styrene) prevented even larger scale grafting but there is no reason to believe that this could not be done without difficulty.

Typical mixing operations are illustrated below for both Cariflex IR 305 and NR.

<u>CX29.PS7.5 LB432:</u> The azo-poly(styrene) was PS7.5L (First Progress Report) which gave a grafting efficiency of 71 per cent with Cariflex IR 305 in the Torque Rheometer. The batch size was increased to improve mixing efficiency and avoid pockets of unmixed poly(styrene) being present at the end of the mixing cycle. The increase had to be achieved by increasing the rubber loading because of the limited amount of poly(styrene) available. The loading was 850g of Cariflex IR 305 and 350g of azo-poly(styrene). Mixing was at speed 1. An initial decrease in power consumption up to 4 min was followed by a very shallow rise to a maximum at 7 min. Antioxidant Nonox WSP (10g) was added at 10 min and mixed for 30 sec. No cooling water was applied and the final recorded temperature was 1 0°C. The mix was withdrawn manually and sheeted on hot two-roll mill. It was very light in colour.

Analysis gave grafting efficiencies of 69 and 67 per cent, results in reasonable agreement with the Torque Rheometer grafting efficiency.

<u>Mix 5L40PS7.5 LB 827:</u> 750g of SMR5L were mixed with 500g of azo-poly(styrene) (RPS6, 9 and 10) at Speed 2 for 6½ minutes. Then the machine was switched off and cooling water turned on. Initial temperature was 70°C and the maximum temperature before turning the water on was 155°C. After a lapse of 4 1/4 minutes, 18g of antioxidant was added and mixed for 1½ minutes. The mix was then discharged. Part of the mix was removed manually. Then it was sheeted on a 2 roll mill (8 passes). Mix temperature by Comark was 157°C. A grafting efficiency of 53 per cent was obtained for the mix. This value is 4 per cent below the value obtained for the mix prepared in the torque rheometer.

The initial series of experiments established three main points:

a) The grafting reaction can be carried out in the BR Banbury with a final grafting efficiency comparable to that obtained in the small scale reactions in the Torque Rheometer.

b) The BR Banbury must be operated at loads in excess of 1 kg to ensure efficient mixing. A load of 1.2 kg appears to be satisfactory.

c) There can be mechanical difficulty in removing the batches from the mixer. The problem is not a serious handicap under the present conditions of operation but a satisfactory solution would simplify the mixing operation considerably.

Table 12 illustrates grafting efficiencies and physical properties for grafts of Cariflex IR 305 (CX Series) and NR (L and 5L series) obtained in the Banbury mixer (LB series) and Torque Rheometer (TR series). Efficiencies tend to be some 3-4 per cent lower in the Banbury mixer but properties are very similar.

2.2.7.2 Compounding In commercial practice styrene butadiene block copolymers are compounded with resins, oils and inert fillers. The three reasons for this compounding are modification of properties, improvement in processability and reduction in cost, with the latter two reasons probably carrying the greater weight. The range of compounding possibilities is very wide and there is a scarcity of published literature on compounding information in relation to specific end uses. It is probable that the most up-to-date cost-effective formulations for any application are known only to the manufacturers directly concerned. Against this background it was necessary to identify some starting point for compounding exercises with NR-poly(styrene) graft copolymers. Processability was taken to be the primary criterion followed by adequate physical properties. Cost effectiveness was not taken into consideration at this stage.

Table 13 gives a composite summary of some general properties of block copolymers compounded for injection moulding applications in footwear. The information is derived from Shell and Phillips and must be regarded as only outline specifications. The compounding ingredients are styrene or other resins, oil, whiting, clay and silica in various combinations.

TABLE 13 PROPERTY SPECIFICATIONS FOR FOOTWEAR APPLICATIONS

MFI (E, 2.16 kg/180°C) g/10 min	5 to 25
Hardness (Shore A)	40 to 60
M300 (MPa)	3 to 5
Tensile strength (MPa)	4 to 7
Elongation (%)	300 to 600

TABLE 12 PHYSICAL PROPERTIES OF GRAFT COPOLYMERS

Mixing Ref. No.	Caloxol on rubber %	Grafting efficiency %	MFI Cond.P g/10 min	M100 MPa	M300 MPa	M500 MPa	M700 MPa	Tensile Strength MPa	EB %
CX 35PS7.5LB614	-	67	0.31	1.97	5.42	9.11	11.7	11.4	620
CX 35PS7.5LB615	-	67	0.89	1.56	3.80	7.34	12.0	12.6	677
CX 40PS7.5LB808	-	75	2.38	2.91	6.54	-	-	8.84	420
CX 40PS7.5TR812	-	78	2.08	2.24	4.54	8.58	13.9	16.2	794
CX 35PS7.5LB825	-	76	0.19	1.58	3.54	7.36	13.4	13.1	682
CX 40PS7.5LB826	-	52	0.52	2.88	6.17	11.3	-	10.7	505
L 40PS7.5LB806	3.0	47	10.9	4.68	-	-	-	8.72	271
L 40PS7.5LB807	3.0	43	3.05	4.16	11.4	-	-	14.3	376
L 40PS7.5TR810	-	20	12 39	1.97	7.39	-	-	15.2	471
L 40PS7.5TR811	3.0	43	2.58	2.29	8.64	19.8	-	20.1	499
5L 40PS7.5TR813	-	47	1.24	2.16	9.27	21.3	-	21.3	438
5L 40PS7.5TR814	3.0	57	1.47	2.65	8.36	20.8	-	19.1	497
5L 40PS7.5LB827	3.0	53	0.26	3.45	11.8	-	-	23.4	450
5L 40PS7.5LB828	3.0	53	0.25	2.87	9.92	22.4	-	22.8	501
5L 40PS7.5LB829	3.0	52	0.29	2.76	8.63	21.4	-	24.3	544

It was found that compounding the NR-poly(styrene) grafts on the BR Banbury was very similar in its ease to the compounding of commercial thermoplastic block copolymers (Third Progress Report, 2.1.7).

However, the supply position with the NR-poly(styrene) graft copolymers precluded extensive compounding work on the Banbury scale but a procedure was developed for small scale compounding in the Torque Rheometer (Third Progress Report, 2.1.7.1). A compound prepared by this procedure from Cariflex TR 4113 block copolymer with styrene resin (36 phr) and napthenic oil (18 phr) gave melt flow properties and tensile strength consistent with data published in Shell Technical Bulletin TRI.2.

Using this small scale compounding procedure the results shown in Table 14 were obtained using Shell 278UL crystal poly(styrene) and Fina 2069 naphthenic oil. Antioxidant Nonox WSP was added to each compound.

TABLE 14 EFFECT OF COMPOUNDING ON PROPERTIES OF NR-POLY(STYRENE) GRAFT

Crystal PS phr	Oil phr	Whiting phr	MFI (E)	M100 MPa	M300 MPa	TS MPa	EB %
38	20	-	6.1	4.1	9.9	10.8	336
30	20	-	11.4	3.6	10.0	11.9	356
20	20	-	11.2	3.0	7.0	9.5	372
30	30	-	26.7	2.0	6.6	10.0	408
30	30	10	21.3	2.7	7.6	10.5	370

The compounds were all prepared from Mix No. LB828 prepared in the Laboratory Banbury (Third Progress Report, 2.1.6). The levels of additives were calculated as parts per hundred parts of total product from the Banbury preparation. Taking the criterion of processability as being of primary importance it can be seen that all the compounds fall within the range of MFI quoted in Table 13 and thus, to a first approximation can be considered to have adequate processability. This processability has been attained with compounds having a considerable reserve of modulus and tensile strength but with only just sufficient elongation at break. If it is assumed that the raw graft copolymer will cost approximately the same as the styrene butadiene block copolymers, the cost effectiveness of the compounds in Table 14 is not satisfactory because the levels of additives used are of the order of one third to one fifth of the levels which can be incorporated into the block copolymers. In terms of meeting minimum requirements of modulus and strength (in the context of the injection moulding applications in footwear) extension of the graft copolymers could occur beyond the limits covered in Table 14 but there is a possibility that the elongation at break may fall to unacceptably low levels. A more precise evaluation of the situation requires a much more extensive evaluation of the compounding variables and this cannot be attempted until a larger and more consistent supply of the graft copolymer is available.

The small scale compounding procedure has also been applied to a preliminary evaluation of different grades of poly(styrene) and poly (alphamethyl styrene) resins as compounding additives. Two batches of NR-poly(styrene) graft copolymer and one batch of Cariflex IR 305 poly (styrene) graft copolymer (Polymers LB828, LB829 and LB825 respectively; Third Progress Report 2.1.6) were used. Resin was added at 25 phr (where phr is defined as above) and each compound also contained 20 phr Fina 2069 oil and 20 phr whiting. The results are summarised in Table 15. The crystal grade poly(styrene)s give higher hardness, M100 and tensile strength than the impact poly(styrene) and also give a slightly higher melt flow index. The alphamethyl(styrene) resins give softer compounds with lower modulus but higher elongation at break and higher tensile strength. They also give considerably higher melt flow indices as might be expected from their low molecular weights. The compounds from the Cariflex IR 305 graft copolymer are all very soft and weak. The modulus advantage which was initially observed for the raw NR graft copolymers becomes even more pronounced on compounding.

TABLE 15 EFFECT OF DIFFERENT COMPOUNDING RESINS

Resin	Resin Type	Graft Copolymer	MFI (Condition E)
BASF Polystyrol 478M	Medium impact	LB828(NR)	18
	poly(styrene)	LB829(NR)	18
		LB825(CX)	30
Shell DG278	Easy flow crystal	LB828	20
	poly(styrene)	LB829	18
		LB825	29
Shell DG277	Extrusion crystal	LB828	24
	poly(styrene)	LB829	22
		LB825	27
Amoco 18-210	Low softening	LB828	53
	poly(alpha-methylstyrene)	LB829	44
		LB825	57
Amoco 18-290	High softening	LB828	45
	poly(alpha-methylstyrene)	LB829	41
		LB825	42

Compound				
M100 MPa	M300 MPa	TS MPa	EB %	Micro hardness
2,63	-	6,72	293	64
2,48	6,59	6,98	320	64
1,08	2,30	2,76	403	37
4,17	-	8,06	250	74
3,78	-	6,84	237	72
1,38	2,62	2,86	358	49
3,63	-	7,78	275	66
3,71	-	8,36	280	73
1,11	2,27	2,99	435	35
1,83	5,17	7,40	390	60
1,83	5,21	7,77	400	60
Too soft to test				
1,87	5,63	7,72	377	55
1,84	5,64	8,23	393	61
Too soft to test				

2.2.8 Extension of the grafting principle to poly(methylmethacrylate) and poly(alphamethylstyrene)

In theory the dry mix grafting route successfully used for poly(styrene) and NR would be applicable to a wide range of other plastics and that differences in T_G, or melting point in the case of crystalline polymers, allied to differences in polarity and compatibility would lead to grafts with NR having changed and possibly superior physical properties. This is of course dependent on the ability to equip the plastic with an azo terminal group, and there being sufficient compatibility of the NR and plastic at suitable mixing temperatures for the grafting reaction to proceed. It was decided that with the limited effort available under the project a suitable extension of the work would be the investigation of poly(methylmethacrylate), because of its polarity and lower compatibility with NR, and poly(alphamethylstyrene) which has a higher T_G than poly(styrene) with at least as high a compatibility with NR.

2.2.8.1 poly(Methylmethacrylate) Although the anionic polymerization of methylmethacrylate using diphenylmethyl sodium as initiator is well established it did not prove possible to obtain a terminal hydroxyl group by reaction of the living polymer carbanion with ethylene oxide as in the case of poly(styrene). As discussed in the Third Progress Report (2.2.6) this appears to be due to the carbanion having a lifetime which is short compared to its reaction time with ethylene oxide. The synthesis of a terminal azo group was therefore precluded.

The only way round this impasse was to resort to the free radical polymerization of methylmethacrylate in the presence of a hydroxyl-containing chain transfer reagent even though this would almost certainly give a product of higher polydispersivity.

Mercaptoethanol is known to have the correct transfer constant to give, using the calculated amount, poly(methylmethacrylate) of ca 10 000 molecular weight with over 90 per cent hydroxyl functionality according to the reaction scheme

$$\text{PMMA}\cdot + \text{HOCH}_2\text{CH}_2\text{SH} \longrightarrow \text{PMMA-H} + \text{HOCH}_2\text{CH}_2\text{S}\cdot$$

$$\text{HOCH}_2\text{CH}_2\text{S}\cdot + n\text{MMA} \longrightarrow \text{HOCH}_2\text{CH}_2\text{S-PMMA}\cdot$$

$$\text{HOCH}_2\text{CH}_2\text{S-PMMA}\cdot + \text{HOCH}_2\text{CH}_2\text{SH} \longrightarrow \text{HOCH}_2\text{CH}_2\text{S-PMMA-H} + \text{HOCH}_2\text{CH}_2\text{S}\cdot$$

Polymerizations were carried out in high vacuum at 60°C using azoisobutyronitrile as initiator.

Table 16 illustrates some typical results showing that polymer yields of up to 70 per cent could be readily obtained with molecular weights close to the calculated value. Silylation of the polymer indicated almost quantitative hydroxyl functionality.

TABLE 16 POLYMERIZATION OF MMA BY CHAIN TRANSFER PROCESS

Polymer	Weight of monomer(g)	Wt.% of mercapto-ethanol	Reaction time(hr)	Conversion(%)	$\overline{M}_n$ (calc)	$\overline{M}_n$ (vpo)	$\overline{M}_w/\overline{M}_n$
M6	94	1.78	12	34	6 879	5 730	1.99
M7	57	1.02	12	70	11 905	13 600	1.74
M8	108	1.01	21	60	11 994	12 000	1.68
M9	379	1.03	16	48	11 905	15 100	1.67
M10	379	1.03	19	45	11 905	12 800	1.92
M11	445	1.76	21	67	7 028	10 200	1.75

More importantly, treatment of the hydroxy polymer in toluene solution with an excess of 2-carbethoxyazocarbonyl chloride gave quite high azo functionalities as shown in Table 17. These were substantiated by the grafting efficiencies to Cariflex IR 305 in solution. Even after 7 days at 60°C the grafting was not quite complete and the figures in Table 17 were raised to virtually the quoted azo functionality by subsequent heating of the solid graft to 150°C for 10 minutes.

TABLE 17 PREPARATION OF AZODICARBOXYLATE TERMINATED POLY(METHYLMETHACRYLATE) USING BROMINE/PYRIDINE OXIDATION OF ACID CHLORIDE

Polymer No.	Scale (g)	Excess acid chloride	Reaction time (hr)	Azo functionality by uv (%)	Solution grafting efficiency (%)
M6.9	2	4	21	82	75
			45	86	
M7.2	1	5	1.5	74	55
M9.3	10	7	2	70	47
M9.6	10	7	2	84	40
M9.7	30	7	2	84	45
M9.8	85	7	2	82	69
M10.4	50	7	2	98	79, 81
M11.10	87	7	2	100	81

The crucial test of dry-mix grafting was also successfully accomplished. The azo-tipped poly(methylmethacrylate) M11.10 of high functionality was mixed in the Torque Rheometer with Cariflex IR 305 at 90°C and 130°C. In both cases the characteristic increase in torque with the onset of grafting was displayed and grafting efficiencies of 27 per cent and 55 per cent respectively were attained. The former value was increased to 43 per cent on heating the product to 150°C for 10 minutes showing that grafting was incomplete at the lower mixing temperature.

Beyond demonstrating that the graft was thermoplastic the physical properties have not been investigated.

2.2.8.2 Adaptation of process to poly(styrene) Although the route to azo-tipped poly(styrene) involving anionic polymerization which has been detailed earlier is very satisfactory it has to be recognised that its implementation on a large scale will require sophisticated chemical engineering. The free-radical polymerization of styrene either in bulk or in emulsion is, on the other hand, carried out widely in industry.

For the sake of completeness, therefore, the route to hydroxyl-tipped polymer via free radical polymerization in the presence of a hydroxyl functionalised transfer agent has been adapted to styrene.

2-Mercaptoethanol has too large a transfer constant in styrene polymerization but an alternative has been found in tribromoethanol. This has a transfer constant of 0.57. By adjusting its concentration and using polymerization conditions identical to those for methylmethacrylate, poly(styrene) samples of molecular weight 6 600, 13 000 and 23 100 have been prepared with conversions from 25 per cent in 25 hours to 44 per cent in 96 hours. Molecular weight dispersions are of course higher than for anionic polymerization, averaging about 1.7. After reaction with azo acid chloride in the usual way, azo functionalities of 90 per cent have been achieved for the poly(styrene).

Provided that the physical properties of NR-poly(styrene) grafts are not impaired by the wider molecular weight dispersion then the free-radical polymerization route will be worthy of consideration when industrial scale preparation of azopoly(styrene) is contemplated.

2.2.8.3 Poly(alphamethylstyrene) Interest in this polymer for grafting to NR was stimulated by its higher T_G (165°C compared to 105°C for poly(styrene)) and the fact that ABA block copolymers prepared from alphamethylstyrene and isoprene have consistently higher moduli and tensile strengths than those prepared from styrene and isoprene.

Poly(alphamethylstyrene) was readily polymerized anionically using n-butyl lithium as catalyst in tetrahydrofuran as solvent although low temperature conditions (-78°C) are required. The living polymer carbanion was terminated with ethylene oxide in the usual way to give hydroxyl functionalities of well over 90 per cent. Treatment with azo acid chloride as for hydroxyl-poly(styrene) produced azo-tipped poly(alphamethylstyrene) with functionalities of 55-75 per cent. The products grafted almost quantitatively to Cariflex IR 305 both in solution and on dry mixing. Table 18 records some typical results. Grafting efficiency was determined by gpc. The products were tough, semi-transparent thermoplastic materials and some physical properties are detailed in Table 19 although no attempt has been made to optimise poly(alphamethylstyrene) content or molecular weight.

TABLE 18 FORMATION OF GRAFT COPOLYMER FROM AZODICARBOXYLATE TERMINATED POLY(ALPHAMETHYLSTYRENE) AND CARIFLEX IR305

Polymer	Functionality (uv, %)	Initial cavity temp(^{o}C)	Mixing time (min)	Final mix temp (^{o}C)	Grafting efficiency (%, dry mix)	Grafting efficiency (%, soln)
PMS1	55	130	5	168	56	49
PMS1	55	130	10	160	52	-
PMS1	55	120	10	155	52	-
PMS3a	77	130	10	152	72	71
PMS3b	67	130	10	155	74	66

TABLE 19 PHYSICAL PROPERTIES OF POLY(ALPHAMETHYLSTYRENE) GRAFTED MATERIAL

poly(alpha-methylstyrene) content (M_n 4500) (%)	M100 (MPa)	M300 (MPa)	M500 (MPa)	M700 (MPa)	Tensile Strength (MPa)	Elongation at break (%)
40	0.81	1.62	2.99	5.25	8.85	949

2.2.9 Problems remaining

The main objectives of the project have been fulfilled but there remain problems requiring resolution before a move to commercial development of the grafting route could be recommended.

2.2.9.1 Variability of capping efficiency The introduction of 2-carbethoxyazocarbonyl chloride to azo-cap hydroxy-poly(styrene) as described in the Third Progress Report (2.4.2) was not only economically desirable but in small scale reactions gave very high capping efficiencies (>80 per cent). The same high efficiencies were initially found when the scale was increased to 1.5 kg of polymer (Third Progress Report, 2.1.2, Table 1). However, as discussed fully in the Fourth Progress Report, 2.1.3, it became apparent as more results were obtained that the large scale capping reactions were variable in efficiency. Thus grafting efficiencies with Cariflex IR 305, a good measure of azo functionality, were respectively 71, 80, 61, 80, 57, 42 and 60 per cent for seven different batches. Because of the lower grafting efficiency for NR it is essential that the functionality of the azopoly(styrene) should not be below 65 per cent and should preferably be 75 per cent or above. This cannot yet be guaranteed.

It is apparent that one reason for the variability is the longer time it takes on the larger scale to isolate and dry the azo-polymer during which time the azo group can be lost by reaction, for example, with hydrochloric acid generated from the azo-acid chloride. Rapid water washing and/or neutralisation of the azo polymer has been found to be beneficial and on still larger scales the necessary introduction of isolation methods such as spray drying or steam stripping could eliminate this source of variability. Further work is still required to be sure that other scale-dependent factors are not causing fluctuations in reaction efficiency.

2.2.9.2 Variation of grafting efficiency with NR In the First Progress Report (Section 2.2.3) it was shown that the non-rubber substances present in natural rubber reduce the grafting efficiency of azopoly(styrene) towards the polymer. The reduced grafting efficiency gives high unbound poly(styrene) levels in the graft copolymer. This unbound poly(styrene) does not contribute to the strength properties and represents wastage of expensive functional poly(styrene).

One way to improve the grafting efficiency is by the deactivation or removal of the interfering non-rubber substances present in NR. There is a large number of different non-rubber substances present in NR, some of which are indigeneous and some of which (eg castor oil) are added during processing of the raw rubber. The amounts of these non-rubber substances vary both within the grades as well as between the various grades of NR. Nitrogen, volatile matter etc are specified for technically specified rubbers. It has been found that there is no direct correlation between the levels of nitrogen, volatile matter and castor oil content and grafting efficiency. A simple example is the behaviour of DPNR towards azo reaction. In general technological terms this rubber is considered to be a purer form of rubber compared to the other grades but it has been found to give much lower grafting efficiencies than SMR 5L. Also a batch of new specification SMR L has been found to give lower grafting efficiency than SMR 5L.

Because of this failure to obtain a correlation between non-rubber contents and grafting efficiency a semi empirical approach has had to be taken to the selection of additives. It is known that certain types of amino compounds and hydroxylic compounds react with the azo function and therefore by treating the rubber with chemicals which could deactivate some of these substances, some improvement in grafting efficiency might be expected. However the additives to be used for treating the rubber have to be either cheap or should be effective at very low concentrations, for the process to be economically attractive and of any practical use.

The additives listed in Table 20 or combinations of some of them were mixed into natural rubber prior to carrying out the grafting reaction. The treated rubber samples were then used for the preparation of graft copolymers containing 40 per cent by weight of poly(styrene) in the torque rheometer under the standard mixing conditions (ie oil temperature setting 90°C, mixing speed 150 rpm and mixing time 15 minutes). Grafting efficiency values for these mixes as determined by gpc analysis of combined and free poly(styrene) contents are given in the Table.

The results show that the grafting efficiency is improved to different extents by the additives. A substantial increase in grafting efficiency was obtained when Caloxol W5G (contains 83.5 per cent calcium oxide dispersed in mineral oil), calcium oxide or magnesium oxide was used as the additive. Of these three additives, Caloxol W5G is preferable, as it could be dispersed easily in rubber and is a proprietary material made specifically for use in rubber compounding. As Caloxol had a pronounced effect in the initial mixing trials, different percentages varying from 1 per cent to 14 per cent were used to determine the concentration of Caloxol that would be necessary to produce the optimum increase in grafting efficiency. From the results, it can be deduced that Caloxol at 3 per cent on rubber is quite adequate to improve the grafting efficiency.

TABLE 20 EFFECT OF ADDITIVES ON GRAFTING REACTION OF AZOPOLY(STYRENE) WITH SMR 5L

Azo-poly(styrene) 40% w/w	Grafting Efficiency % with Cariflex	Additive		Grafting Efficiency % with NR
		Type	Conc^n on NR %	
A	72.5	-	-	40.0
A	"	TDI dimer	1.5	48.0
A	"	Zinc oxide	3.1	44.0
A	"	Caloxol W5G	6.5	53.0
A	"	Hisil	6.5	44.0
A	"	Devolite Clay	6.5	42.0
A	"	Whiting	6.5	43.0
B	77.2	-	-	42.0
B	"	Boric acid	3.1	49.0
B	"	Zinc oxide	6.5	50.0
B	"	Caloxol W5G	1.0	56.0
B	"	Caloxol W5G	2.0	57.0
B	"	Caloxol W5G	3.1	58.0
B	"	Caloxol W5G	6.5	58.0
B	"	Caloxol W5G	10.0	59.0
B	"	Caloxol W5G	14.0	59.0
C	82.6	Caloxol W5G	3.0	63.0
C	"	Caloxol W5G	3.0	59.0
C	"	Caloxol W5G	3.0	67.0
D	85.0	Caloxol W5G	3.0	69.0
E	78.0	-	-	52.0
E	"	Caloxol W5G	3.0	61.0
E	"	Calcium oxide	3.0	61.0
E	"	Magnesium oxide	3.0	61.0
E	"	Dicyclohexyl carbodiimide	1.0	56.0

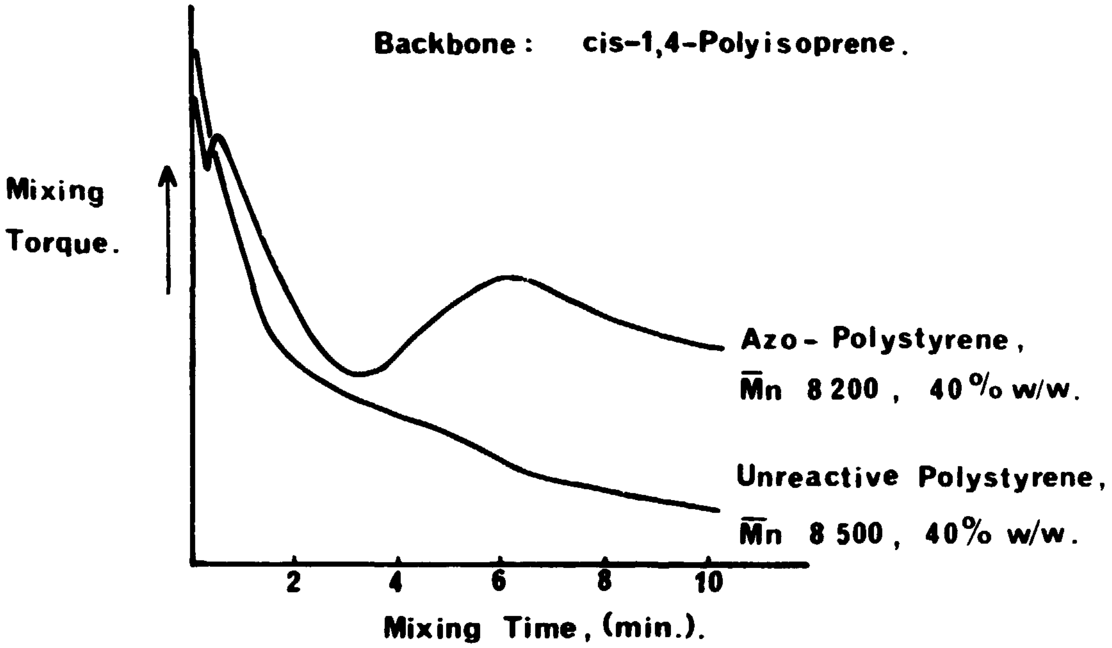
It has also been found that there is no further improvement when combinations of additives were used. On the contrary, in certain cases it has been found that the combined effect of two additives was lower than the effect of Caloxol alone. Although a substantial increase in grafting efficiency was obtained by Caloxol treatment, there is still about 15-20 per cent difference between the grafting efficiencies obtained with Cariflex IR 305 rubber and treated natural rubber.

Experiments on various grades of NR have shown that SMR 5L and SMR 10 respond well to this treatment. Further, these rubbers were found to be the most suitable grades of NR (even without the Caloxol treatment) for carrying out grafting reaction. With this improvement it has now become possible to prepare natural rubber graft copolymers with high grafting efficiencies (about 60 per cent using azopoly(styrene) of about 80 per cent functionality). Caloxol has no effect on the grafting efficiency in Cariflex showing that it acts only on the detrimental non-rubbers in NR and does not catalyse the azo addition reaction.

Recent work has shown that one effect of the interfering non-rubber(s) is to produce free poly(styrene) having simple multiples of the molecular weight of the azopoly(styrene). This does not happen in Cariflex and is reduced in NR by the presence of Caloxol. Such a clue to the mode of action of the interfering substances may lead to their positive identification and thence to ways of removing them from NR or nullifying their effect more efficiently than by Caloxol.

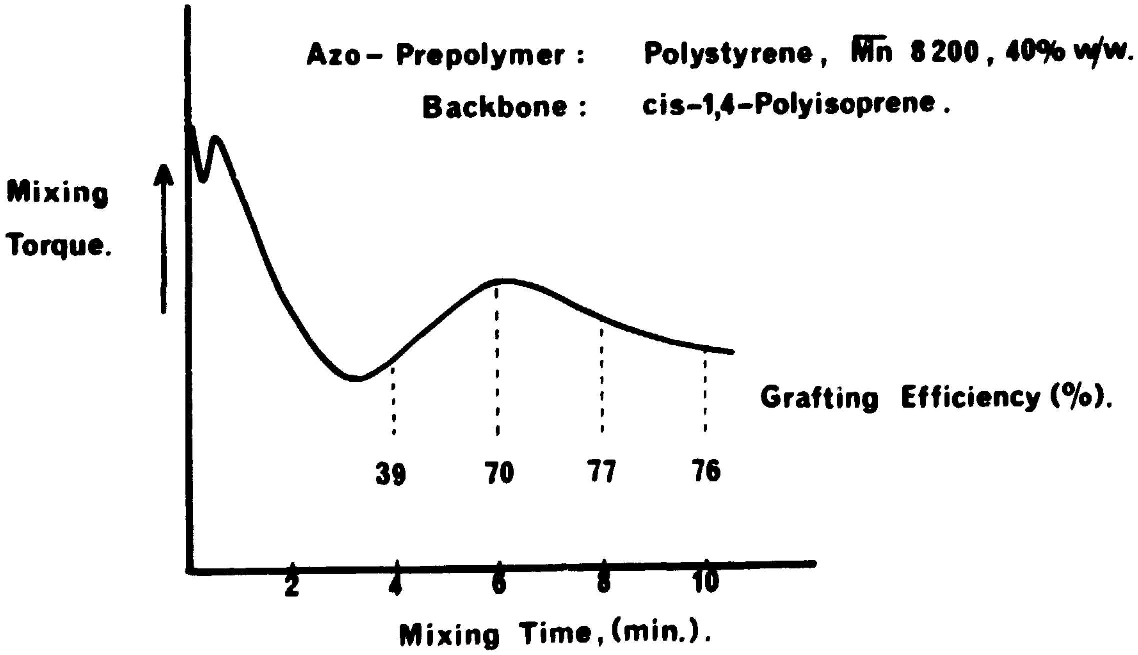
Graft Copolymer Formation in an Internal Mixer (Dry Mix).

2. Figure 1



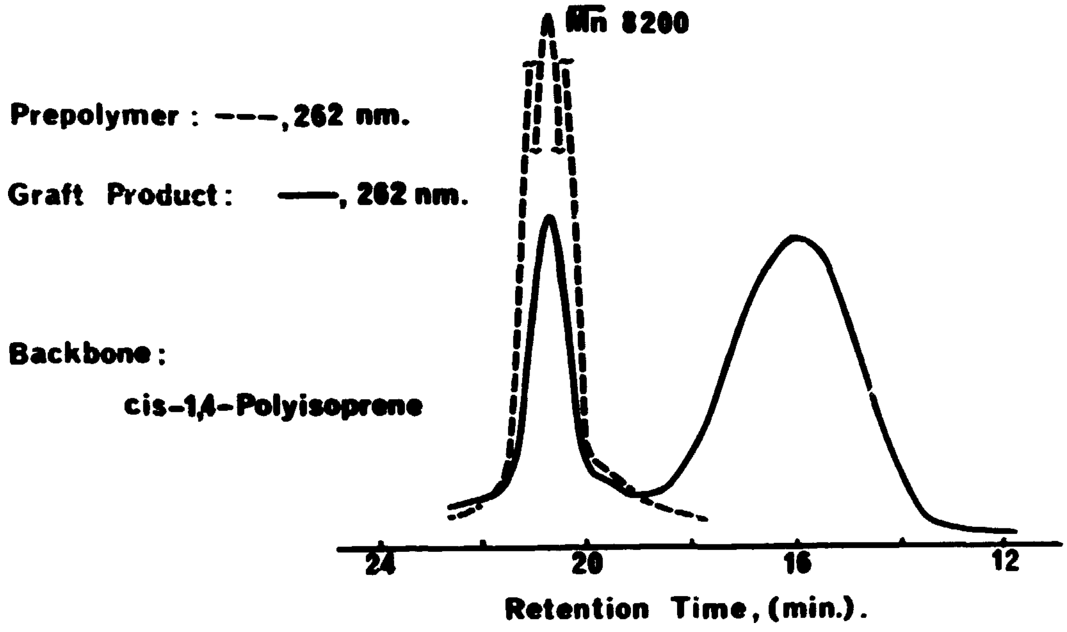
Grafting Efficiency During Mixing.

2 Figure 2



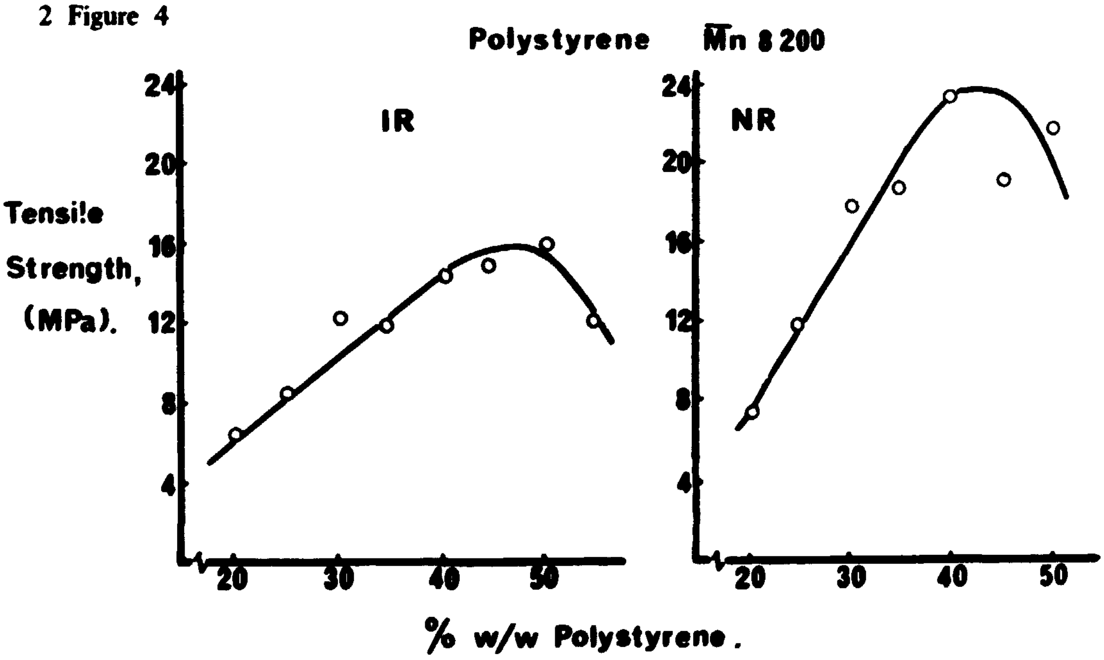
G.P.C. of Styrene Graft Copolymer (Dry Mix).

2 Figure 3



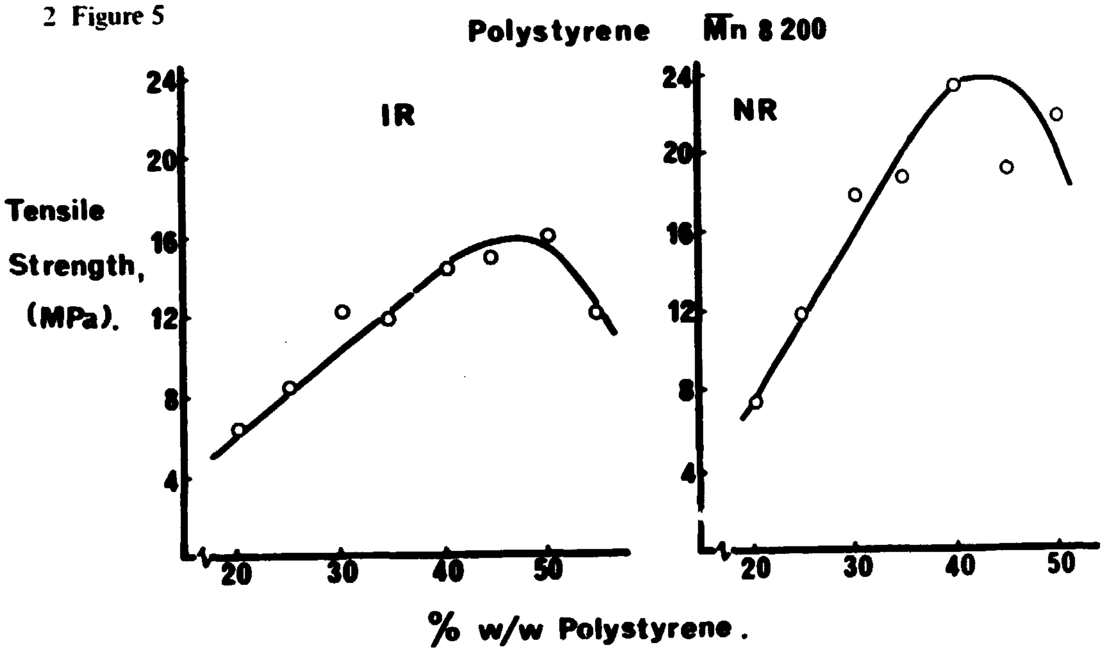
Variation of Tensile Strength with Polystyrene Content (Dry Mix).

2 Figure 4

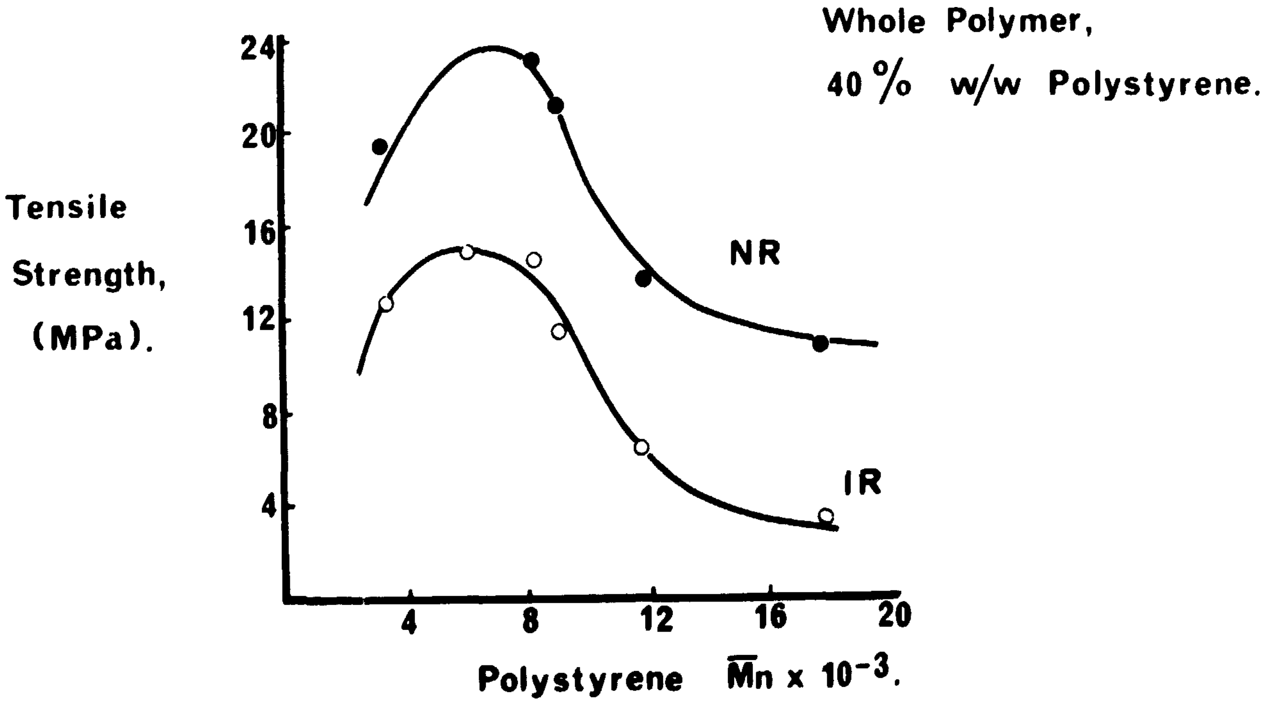


Variation of Tensile Strength with Polystyrene Content (Dry Mix).

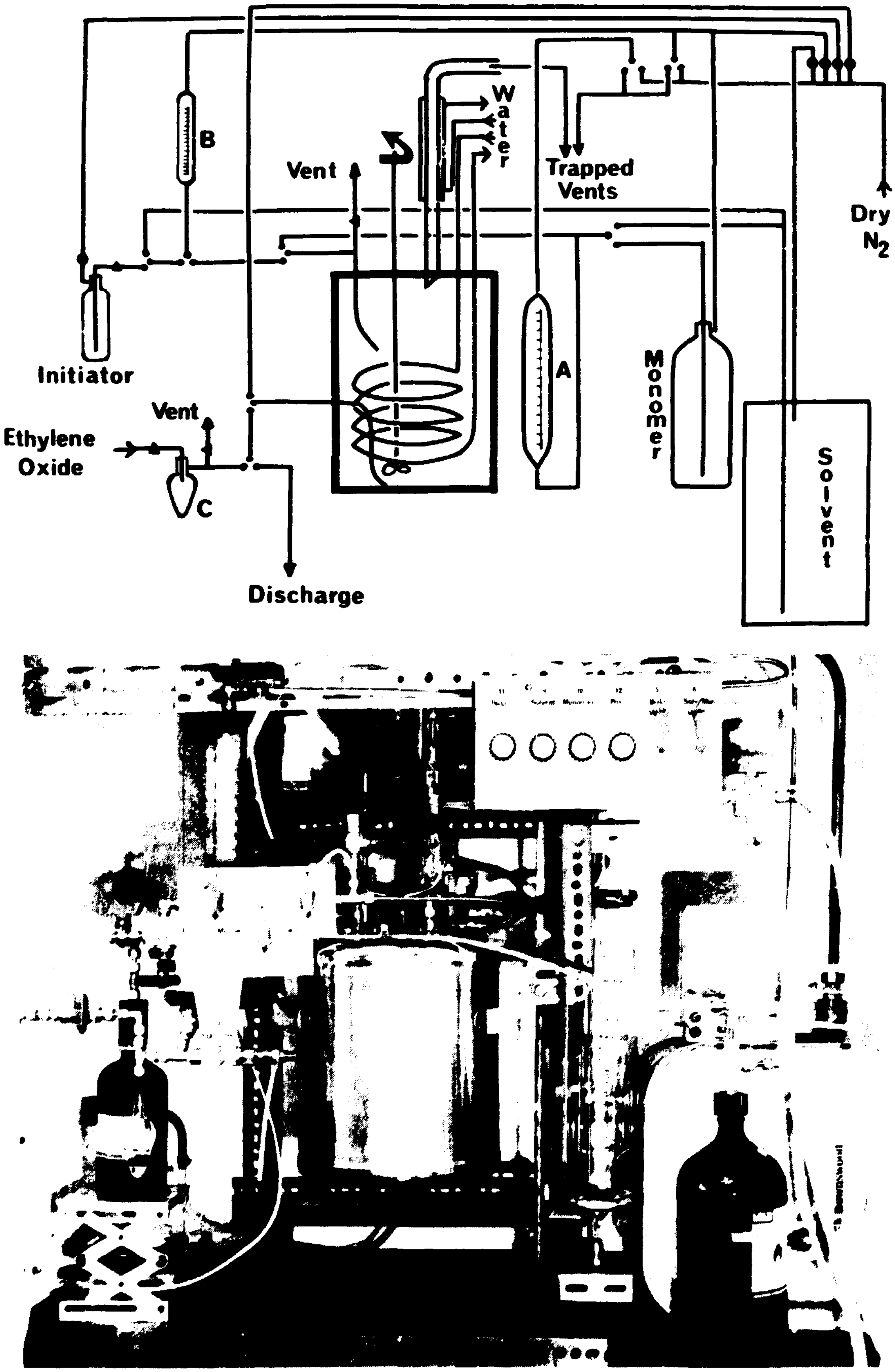
2 Figure 5

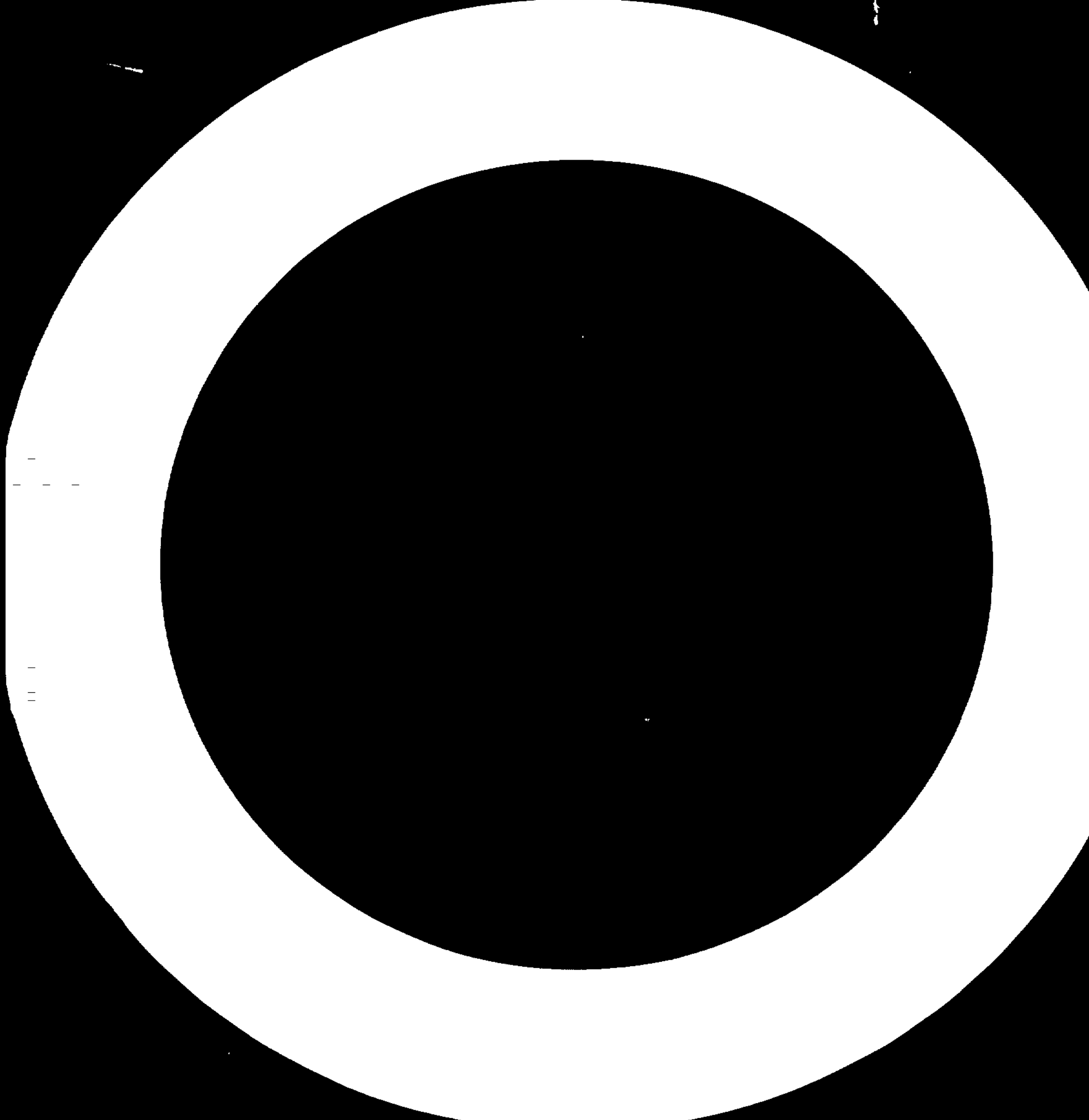


Variation of Tensile Strength with Polystyrene Molecular Weight (Dry Mix).



2. **Figure 6** Schematic diagram and photograph of stainless steel polymerization reactor.





3 THERMOPLASTIC NATURAL RUBBER BLENDS

3.1 INTRODUCTION

3.1.1 Concept

Originally it was believed that a thermoplastic rubber would need to be a copolymer or graft of a hard plastic and a rubber in which rubber chains were 'crosslinked' at ambient temperatures by domains of the hard material. More recently, there has come onto the market a number of thermoplastic rubbers which are simple physical blends, mostly based on the synthetic rubber EPDM and a polyolefin, such as poly(propylene). The rubber may be unvulcanized, partially vulcanized or fully vulcanized. Such materials are cheaper and simpler to make than the copolymer thermoplastic rubbers; they tend to be harder and represent a half-way house between plastics and true rubbers. They have already established fast-growing markets in automotive body components (eg bumpers) and their success in these is leading to wider usage in a variety of moulded and extruded products.

Recognizing the desirability of establishing a niche for NR in this expanding market, MRPRA had previously carried out a brief feasibility study. This showed that blends of NR and poly(propylene) (PP) could be easily prepared and that they appeared to match the overall properties of wholly synthetic blends; they could readily be moulded (eg by injection moulding); their stiffness could be adjusted by varying the blend composition; they could readily be painted (an important consideration for the main applicational area envisaged: automotive body components) and ageing behaviour was excellent even on exposure to ozone.

3.1.2 Implementation

The taking of the concept to a practical reality required four main lines of attack.

(i) Optimization of blend formulations for processing behaviour and physical properties

(ii) Demonstration of feasibility of large (tonnage) scale production and finding potential commercial producers

(iii) Assessment of the economics of production in various locales

(iv) Stimulation of interest among potential users by sampling and trial production of specific applications

3.1.3 Outcome

The composition of thermoplastic blends of NR and PP (TPNR) has been developed to meet the property requirements (specified or infered) for a number of applicational areas. Much experience has been gained of processing behaviour in injection moulding and extrusion using a variety of types and sizes of equipment and blend compositions have been adjusted to give optimum results for specific conditions.

Considerable experience has been gained relevant to the large-scale factory production of TPNR blends, culminating in production trials (50 kg batch weight) in the factory of a UK custom compounder. Production has also been carried out by the RRIM in Malaysia. The blending operation, in a standard rubber internal mixer, is simple and no problems have been encountered. There is no obstacle, therefore, to tonnage scale production of TPNR blends.

Estimates of material and production costs in Europe (specifically in the UK), indicate that the commercial selling price for TPNR blends could undercut that for comparable synthetic products by 15-20 per cent. Estimates of production cost in an NR producing country (specifically Malaysia) show the expected influence of lower labour and depreciation charges and the lower cost of NR (duty remission and absence of freight costs) makes the overall competitive position of TPNR blends even more attractive.

Considerable interest has been aroused in a number of applicational areas. The main promotional effort has been on automotive components, including production trials for the bumpers of a Scandinavian car. Footwear (soling) is another promising area and it is significant to note that the RRIM was successful in persuading an international footwear company to put an RRIM-produced TPNR blend into production trials for its local operation. Other applications currently undergoing development include: rail pads (under test by a European railway network); linings for chemical plant (an international chemical company has accepted a TPNR blend as meeting their specification for chemical resistance); products for the dairy industry; stair nosings and irrigation hose.

In summary, TPNR blends have been developed to the stage where large-scale production and use is feasible; blend compositions can readily be tailored to meet the needs of individual applications and processing conditions. TPNR blends could be produced very economically in the West (ie from imported NR), though it should be said that this will probably not apply in the USA where governmental policies concerning oil prices cause the prices for all plastics and synthetic rubbers to be low by world standards. Export of TPNR blends from NR producing countries can certainly be considered, and of course the material would be of exceptional interest for domestic use in those NR producing countries which are actively encouraging local manufacture of plastics and rubber products for which TPNR blends could readily compete with imported synthetic materials.

3.1.4 Problems relevant to further implementation

These are minor. In some circumstances TPNR blends have an unpleasant odour, more significant during processing than in use. This can be ameliorated in various ways but may be a disqualifying factor where odour is totally unacceptable. Some problems have also been found in contriving a satisfactory surface appearance of mouldings, but these have been overcome after detailed adjustments to blend composition and/or processing conditions.

3.2 BODY OF REPORT (THERMOPLASTIC BLENDS)

3.2.1 Optimisation of properties and processing

3.2.1.1 Physical properties The physical properties such as tensile strength, elongation at break and modulus which are routinely measured for vulcanizates are not of critical importance for thermoplastic blends since the applicational requirements are not high. Table 1 illustrates the physical properties of some of the early TPNR blends compared with those of synthetic competitors. It can be seen that even at this stage of development the TPNR properties were not inferior and were quite adequate to meet typical automotive component specifications. Thus, little optimisation of these basic properties was required.

Perhaps the most important attribute of these harder thermoplastic rubbers is their stiffness or flexural modulus. The stiffness of TPNR blends depends on the relative proportions of the two polymers and also on the direction in which test pieces are cut relative to the direction of flow in the mould. Figure 1 shows the effect of PP content on flexural modulus for blends ranging from 75/25 NR/PP to pure PP. A practically useful range is from 75/25 to about 15/85 NR/PP. The former is a material with similar properties to sole crepe (which relies on crystallized rubber for its reinforcement) whilst the latter is similar to impact resistant poly(propylene).

Between these limits are blends that may be suitable for automotive applications such as flexible filler panels and bumper components. These products form part of systems designed to prevent damage to the vehicle in low speed collisions. The material must be stiff enough for the component to retain its shape in all weather conditions from -30° to +70°C and to withstand distortion during paint baking at 120°C, where this is applicable. TPOs and TPUs are being used in these applications and the physical properties of TPNR blends suggest that they also will meet these requirements of the car industry.

Tensile strength and elongation at break are also markedly dependent on PP content.

Initially, partial crosslinking of the NR was carried out during the blending operation by the addition of a small amount (0.3 phr) of dicumyl peroxide (Dicup). This had a beneficial effect on the processing properties of blends containing a major proportion of NR as was described in the First Progress Report (2.5). It was also pointed out that dicumyl peroxide reaction products give an unpleasant odour to the material and that peroxy radicals are likely to initiate oxidation of the propylene. To these two possibly undesirable features may be added a third. This is that the addition of the peroxide, while perfectly acceptable in a batch process using an internal mixer, may not lend itself easily to a continuous process based on extrusion mixing because of the necessity to add the peroxide (and later, antioxidant) at timed intervals after the commencement of polymer blending and also because of the requirement that gaseous

TABLE 1 PROPERTIES OF TPNR BLENDS AND VARIOUS TPO MATERIALS

	TPNR 6040	TPNR 4060	UNIPRENE 910	VISTAFLEX 911	TPR 1900	TPNR 6040/ 45	TPNR 4060/ 45	VISTAFLEX 916C	TPV-F	NORDEL 301G	Ford Specification Medium modulus grade	Ford Specification High modulus grade
Manufacturer	-	-	ISR	Esso	Uniroyal	-	-	Esso	Exxon	DuPont	-	-
Colour	Natural	Natural	Natural	Natural	Natural	black	black	black	black	black	black	black
Density, g/cm^3	0.91	0.91	0.88	0.89	0.88	1.08	1.08	0.95	1.05	1.02	-	-
Flexural modulus at 23°C,MPa	370	730	-	220	240	400	880	200	190	230	138 to 345	>345
Ratio of modulus at -30°C to modulus at 70°C	8.9	7.4	-	-	-	8.3	6.7	-	9.6	9.1	12*	8*
Tensile strength, MPa	13	18	14	11	13	13	14	8	6	15	> 6.9	> 10.4
Elongation at break, %	190	330	250	280	250	110	40	240	100	120	>70	> 70
[illegible] ohm cm	$>10^{15}$	$>10^{15}$	$>10^{11}$	$>10^{16}$	-	80	2.5×10^{2}	60	1.1×10^{8}	-	$<1\times10^{9}$	$<1\times10^{9}$

* For information only. Not a requirement.

reaction products would have to be vented from the extruder in order to maintain efficient mixing.

Since extrusion blending is a technique widely used in the plastics industry it was felt that consideration should be given to this procedure as an alternative method of preparing TPNR blends. For these reasons a number of batches of TPNR were prepared in a laboratory sized Banbury mixer in which four different crosslinking systems were investigated. A further reason for carrying out this study was that a recent patent claims that an elastomeric thermoplastic composition comprising a blend of crystalline thermoplastic resin and a fully dynamically vulcanized high unsaturation diene rubber (including NR) has superior physical properties when compared with blends containing uncrosslinked rubber. Compositions of the batches and physical properties of injection moulded sheets are given in Table 2. The data show that mix B, having a low state of vulcanization, has higher strength and elongation than A (unvulcanized), but fully vulcanized mixes C and D have no significantly better tensile strength than B while their elongations are lower. Similarly, optimum properties are given by a level of 'Novor' (mix F) that is below the amount required to fully vulcanize NR and finally the properties of TPNR 5050 (in this nomenclature the first two digits represent the NR content, parts per hundred of polymer, and the last two the PP content) are hardly affected by a more than three-fold increase in dicumyl peroxide level (H to J). Systems D and F may be appropriate ones to study in the extrusion blending operation referred to above, because with these systems (a) there is no necessity to delay addition of antioxidant until crosslinking is complete and (b) there should be no gaseous reaction products, other than traces of water which could be absorbed by adding a few percent of a calcium oxide dispersion such as Caloxol.

The molecular weight of the poly(propylene) in blends was determined by extracting it in boiling xylene and recrystallizing, dissolving it in decalin at 135°C and measuring the intrinsic viscosity of the solution.

An alternative peroxide crosslinking agent, Perkadox 14/90, was later investigated as this gave less odourous decomposition products than the acetophenone from Dicup. Properties such as impact strength, yield stress, flexural modulus, hardness and, for processability, melt flow index (MFI)

TABLE 2 THERMOPLASTIC NR BLENDS WITH DIFFERENT CROSSLINKING SYSTEMS

		A	B	C	D	E	F	G	H	J
SMR L		60	60	60	60	65	65	65	50	50
'Propathene' GWM 22		40	40	40	40	35	35	35	50	50
Dicumyl peroxide			0.36						0.3	1.0
MBTS				0.9	0.6					
HVA-2				4.5						
TMTD					1.2					
ZnO					3					
Stearic acid					0.6					
Sulphur					1.2	0.026	0.052	0.078		
'Novor' 924						1.3	2.6	3.9		
ZDMC						0.4	0.8	1.2		
Flectol H		1	1	1	1					
Antioxidant 2246						1	1	1	1	1
Rheometer torque at 180°C		5	7	20	22	9	15	14		
Tensile strength, MPa	(a)	11.3	13.5	15.8	15.2	11.8	13.5	13.5	16.4	16.3
	(b)	8.0	16.2	17.1	15.1	11.4	16.0	15.8	18.8	16.0
Elongation, %	(a)	55	140	105	75	70	80	90	360	305
	(b)	450	525	305	360	340	445	395	550	550
Stored energy at break,	(a)	3.6	12.6	9.5	5.6	4.3	6.0	7.1		
MJm^{-3}	(b)	16	36.1	26.2	27.5	16.5	29.8	28.0		
M_w of PP, x 10^{-5}		2.5	1.6	2.4	2.3		2.3			

(a) in radial direction (b) perpendicular to radial direction are very important for thermoplastic blends used for the production of automotive products, eg impact resisting bumpers and other semi-rigid components. The effect of Dicup, Perkadox and other crosslinking agents on these properties for a range of blend compositions is given in Table 3.

One kilogram batches were made in a BR Banbury mixer, sheeted on a two-roll mill and, when cold, granulated in the Blackfriars rotary machine using an 8 mm diameter screen. Test pieces were prepared using the Arburg 220 injection machine and a tool to provide a variety of moulded test samples simultaneously.

The compositions were NR/PP = 40/60, 30/70, 25/75, 20/80, 10/90 and crosslinking systems were used at two levels, both of which, however, were sufficient only to partially crosslink the rubber phase. Without crosslinking the MFI increases slightly as the rubber content decreases. At the two lowest levels (20/80 and 10/90) the MFI is higher than that of the PP itself. This could be due to oxidation of PP. Crosslinking reduces MFI most markedly in blends with relatively high rubber contents and, of course, when higher levels of crosslinking agents are used. There is a counter-effect with peroxide, however, shown by higher MFI values for 10/90 blends which again is due to degradation of the PP.

There are rough correlations between flexural modulus and cold impact strength, with some indication that a degree of crosslinking toughens the material, but the data is too scattered to show which crosslinking system is most beneficial.

3.2.1.2 Ageing behaviour Accelerated air-ageing of TPNR blends proved to be quite adequate for service requirements and surprisingly similar to synthetic TPR blends based on EPDM (Table 4).

TABLE 4 AGEING OF TPNR COMPARED WITH TPR

	UNAGED			AGED 3 DAYS AT 100°C		
	M100 (MPa)	TS (MPa)	EB (%)	M100 (MPa)	TS (MPa)	EB (%)
TPNR*	11.0	11.8	108	10.2	10.6	140
TPR (Uniroyal)	11.0	1.8	176	13.3	13.3	120

*SMR 5L 65, PP HF20 35, Dicup 0.39, Antioxidant 2246 1

TABLE 3 EFFECT OF CROSSLINKING ON PHYSICAL PROPERTIES OF TPNR

NR/PP ratio	MFI (230°C/ 2.16 Kg, g/10 mins)	Shore D	Yield stress[1], MPa	Yield stress[2], MPa	Flex mod, MPa	Izod, J/m	
						23°C	cold[3]
No crosslinking							
40/60	3.8	56	21	18	560	NB	98
30/70	3.6	62	26	23	730	NB	82
25/75	3.6	65	28	26	820	NB	76
20/80	4.5	67	31	28	890	169	66
10/90	5.5	70	35	32	1 100	142	38
Partial crosslinking with Perkadox 14/90, 0.25 phr							
40/60	0.5	56	19	17	590	NB	NB
30/70	1.1	63	24	21	690	NB	NB
25/75	2.3	64	27	24	830	NB	147
20/80	4.4	66	29	26	870	NB	87
10/90	5.1	70	34	31	1 080	142	38
Partial crosslinking with Perkadox 14/90, 0.5 phr							
40/60	0.3	56	20	18	620	NB	NB
30/70	0.9	63	23	21	640	NB	NB
25/75	1.9	64	25	22		NB	153
20/80	1.8	66	26	23	800	NB	169
10/90	6.7	71	35	30	1 090	142	44
Partial crosslinking with sulphur system, low level[4]							
40/60	1.4	60	24	20	720	NB	218
30/70	2.4	67	26	24	770	NB	98
25/75	2.4	69	29	26	910	NB	120
20/80	4.4	71	32	29	930	120	49
10/90	4.4	72	37	33	1 150	158	38
Partial crosslinking with sulphur system, higher level[5]							
40/60	0.2	60	26	24	630	NB	NB
30/70	0.8	66	28	26		NB	NB
25/75	1.1	69	29	26	880	NB	158
20/80	1.4	70	32	28	940	NB	120
10/90	3.4	73	37	33	1 000	158	60
PP[6]	4.0	74	-	34	1 700	82	27(-20°C)

[1] Extension rate 500 mm/min

[2] Extension rate 50 mm/min

[3] -25°C, approximately

[4] Sulphur 0.13 phr, MBT 0.13 phr, TMTD 0.25 phr, ZnO 1 php, Stearic acid 0.25 php

[5] Sulphur 0.25 phr, MBT 0.25 phr, TMTD 0.5 phr, ZnO 2 php, Stearic acid 0.5 php

[6] Data in manufacturer's publications

NB: No break

A more extensive screening of antioxidants and combinations of antioxidants used for both NR and PP was undertaken in respect of air ageing and outdoor weathering.

A total of fifteen batches of TPNR 5050 were prepared in the BR Banbury, all containing 0.9 to 1% added antioxidant, but differing in that this antioxidant was composed of 1) a phenolic type only, 2) a combination of phenolic, uv absorber and a synergist (dilauryl- or distearyl-thiodipropionate) and 3) a combination as in 2) plus an organic compound containing phosphorous. One series of mixes contained 0.5 phr Dicup R and one contained no crosslinking agents.

Details of the various antioxidant combinations and tensile properties before and after air oven ageing for 7 days at 100°C are given in Table 5. The latter were measured on injection moulded dumb-bells having maximum polymer orientation effects, due to flow, along the dumb-bell. The results show that the tensile strength of TPNR 5050 made without a crosslinking agent is fully retained or even increased after ageing. Elongation at break decreases, however. In the case of TPNR containing peroxide there is a loss of both tensile strength and elongation at break after oven ageing.

No single antioxidant proved to be outstanding and the best tensile retention was given by combinations, particularly of Good-rite 3114, Irganox PS802 and Tinuvin 327.

For the weathering tests disc shaped samples were injection moulded and then placed outdoors in a south facing direction at an angle of 45° for approximately 3 months (December to March). All the discs prepared from the blend containing Dicup as crosslinking agent whitened at the surface whereas those containing no Dicup were undamaged and had a good surface appearance. Later work showed that the use of a sulphur crosslinking system also did not give the whitening on weathering. Analytical results using the scanning electron microscope discussed in the Fourth Progress Report (2.5.3.1) show that the whitening is due to the formation of a porous layer of oxidised and degraded PP from which NR is absent to a depth of 2-5 µm. It may be that the Dicup initiates oxidative degradation of the PP which, in sunlight, can catalyse the profound degradation of the surface NR.

It is known that TPNR blends at the softer end of the hardness range need a partially crosslinked rubbery phase for optimum physical properties. However, the above exposure tests and oven ageing results show clearly that dynamic crosslinking by peroxide can be detrimental to TPNR 5050. There is sufficient poly(propylene) in TPNR 5050, and grades with lower rubber content, for the poly(propylene) to form a continuous phase. Whether the rubbery component is partially crosslinked or not is probably not of very great importance, but if some crosslinking is to be introduced a non-peroxide system would be preferable.

Resistance to ozone cracking by TPNR blends, even those containing 60 per cent of NR, is extremely good and no difficulty has been found in meeting all the necessary specification tests without the addition of waxes or chemical antiozonants. Figure 2 illustrates the complete lack of cracking under strongest test conditions.

3.2.1.3 Painting procedures Components such as bumpers, panels and facias for cars will often require to be painted to match the metal finish of the car. NR itself is readily painted with flexible polyurethane paints after a simple chlorine water dip or wipe to ensure good adhesion.

With the TPNR blends two problems had to be overcome before painting could be regarded as a routine operation.

The first was the question of paint adhesion. For NR contents of below 50% the chlorine water treatment was inadequate to ensure good adhesion and samples failed the cross-hatch adhesion test and also blistered on exposure trials in Florida. The use of Seibert Oxidermo AP-100C as a flash primer completely overcame this difficulty for all blend compositions. Painted specimens have now passed the official 1 year Florida exposure tests with no colour tone change, no surface crazing, no cracking when bent and retention of over 80 per cent gloss after cleaning.

The second problem was concerned with the frequent use in the car and related industries of electrostatic spray painting techniques which required that the TPNR blend should be conductive.

The required conductivity can be achieved by incorporation of appropriate amounts of the so-called conductive blacks or of other grades, such as high-structure HAF black.

TABLE 5 EFFECTS OF PEROXIDE CROSSLINKING AND OF VARIOUS ANTIOXIDANTS ON THE AGEING PROPERTIES OF TPNR 5050

TPNR 5050	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Dicup R	0.3	0.3	0.3	0.3	0.3	0.3	-	-	-	-	-	-	-	-	-
Permanax WSO	1.0	0.3	0.3	-	-	-	1.0	0.3	0.3	-	-	-	0.3	-	-
Good-rite 3114	-	-	-	1.0	0.3	0.3	-	-	-	1.0	0.3	0.3	-	0.3	0.2
Irganox PS800	-	0.3	0.3	-	0.3	0.3	-	0.3	0.3	-	0.3	0.3	-	-	-
Irganox PS802	-	-	-	-	-	-	-	-	-	-	-	-	0.3	0.3	0.2
Tinuvin 327	-	0.3	-	-	0.3	-	-	0.3	-	-	0.3	-	0.3	0.3	0.3
Tinuvin 770	-	-	0.3	-	-	0.3	-	-	0.3	-	-	0.3	-	-	-
Polygard	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2
<u>Unaged</u>															
TS, MPa	16.6	16.5	16.3	15.7	15.6	15.7	17.4	16.7	17.1	16.7	16.3	16.4	17.1	17.5	17.4
M50, MPa	15.5	15.2	15.4	14.7	14.8	14.7	17.7	17.2	17.5	17.3	17.0	17.0	17.5	18.1	16.0
M100, MPa	16.1	15.9	16.2	15.3	15.4	15.3	-	17.0	-	17.0	17.0	-	-	17.6	17.4
EB, %	200	235	195	250	220	255	90	100	95	105	100	90	95	105	110
<u>Aged 7 days at 100°C</u>															
TS, MPa	13.7	13.4	13.1	12.8	12.7	11.8	18.8	18.4	18.1	17.1	17.8	18.4	19.8	20.9	20.7
M50, MPa	14.3	14.0	13.8	12.3	13.2	12.2	-	-	-	-	-	-	-	-	-
EB, %	95	105	95	75	95	85	60	45	40	40	43	40	45	40	40

Figure 3 shows the effect of concentration of three grades of black on the resistivity of TPNR blend 6040. The curves are of similar shape to those given by vulcanized rubber containing these blacks and it is clear that in the antistatic region resistivity is very sensitive to concentration of black and also to (not shown) the degree of dispersion of the black.

It was found that two methods of measuring conductivities did not always give the same values, and in particular it was claimed by one supplier of automotive components that several samples of TPNR believed to be antistatic by reference to Figure 3 were not conductive enough for electrostatic spraying. Therefore selected proportions of the two blacks HAF N347 and the highly conductive Ketjenblack EC were compared with increased amounts of the N347 in their effects on resistivity. Taking into account other effects of carbon black, such as its influence on flow and elongation at break, it was concluded that the optimum combination consisted of 40 parts N347 and 5 parts Ketjenblack.

Quantities of TPNR 6040 and 4060 (ie 60/40 and 40/60 NR/PP blends respectively) containing these amounts of black were prepared and injection moulded sheets have been electrostatically spray painted with flexible urethane paints of the brand currently used in the USA automotive industry for painted flexible body panels and have successfully passed the Florida exposure tests.

3.2.1.4 Optimisation of processability Trial mouldings of Saab bumpers from TPNR 60/40 by Scandia Fabriken (see later) on a Demag 1250 tonne injection moulding machine showed that although mould filling was satisfactory, the surface appearance of the bumper was marred by a mixture of shiny and dull areas to give a kind of water-marking. The sample of TPNR supplied had been dynamically crosslinked during its preparation with 0.15 parts of Perkadox 14/90 and it was suspected that the low value of the melt flow index resulting (less than 1) could be responsible for the processing deficiency. The TPR currently used for the bumper, Vistaflex 911, has an MFI of 12.5 and gives a good surface finish. Other TPRs of lower MFI were unsatisfactory.

Attention was paid to the raising of the MFI of TPNR. Omission of the crosslinking agent gave an MFI of 5.0; this improved the surface but it was still unsatisfactory.

Other methods of increasing melt viscosity without affecting the modulus were investigated in order to arrive at a material more suitable for Saab bumpers.

Two approaches were taken: (1) use of lower molecular weight grades of PP, and (2) addition of plasticizers. Also, PP copolymer grades were compared with PP homopolymers and the effect of increasing the filler content was determined.

Table 6 gives a number of formulations with different grades of PP each containing 2 parts of black. These mixes were injection moulded into a 2 mm deep square shaped mould having a fan gate on one side. With this mould flow is mainly undirectional. A subjective assessment of surface appearance was made and the melt flow index (MFI) of each mix measured.

TABLE 6 TPNR BLENDS USING PP HOMOPOLYMERS AND COPOLYMERS

SMR L	60	55	60	60	55	55
PP homopolymer [1]	40					
PP homopolymer [2]		40				
PP homopolymer [3]			40			
PP copolymer [4]				40	40	45
Atactic PP		5			5	
HAF black	2	2	2	2	2	2
Antioxidants	1.25	1.25	1.25	1.25	1.25	1.25
MFI of the PP [5]	0.5	4	8	4	4	4
MFI of the blend [5]	0.4	1.3	1.6	0.8	1.1	1.0
" " " " [6]	2.3	6.9	6.5	3.2	5.0	4.4
Flexural modulus, MPa	170	240	290	260	250	270
Surface texture	strain marks	flow mar	flow marks	slight flow marks	slight flow marks	slight flow marks

1. Shell's PLZ 423
2. ICI's GWM 22
3. Shell's RM 6100
4. Shell's KMT 6100
5. At 230°C with 2.16 Kg load
6. At 230°C with 5.0 Kg load

None of these mixes had the very pronounced wavy flow pattern over the whole of the sample as found previously with partially crosslinked TPNR 6040 which had a very low MFI (<1.0).

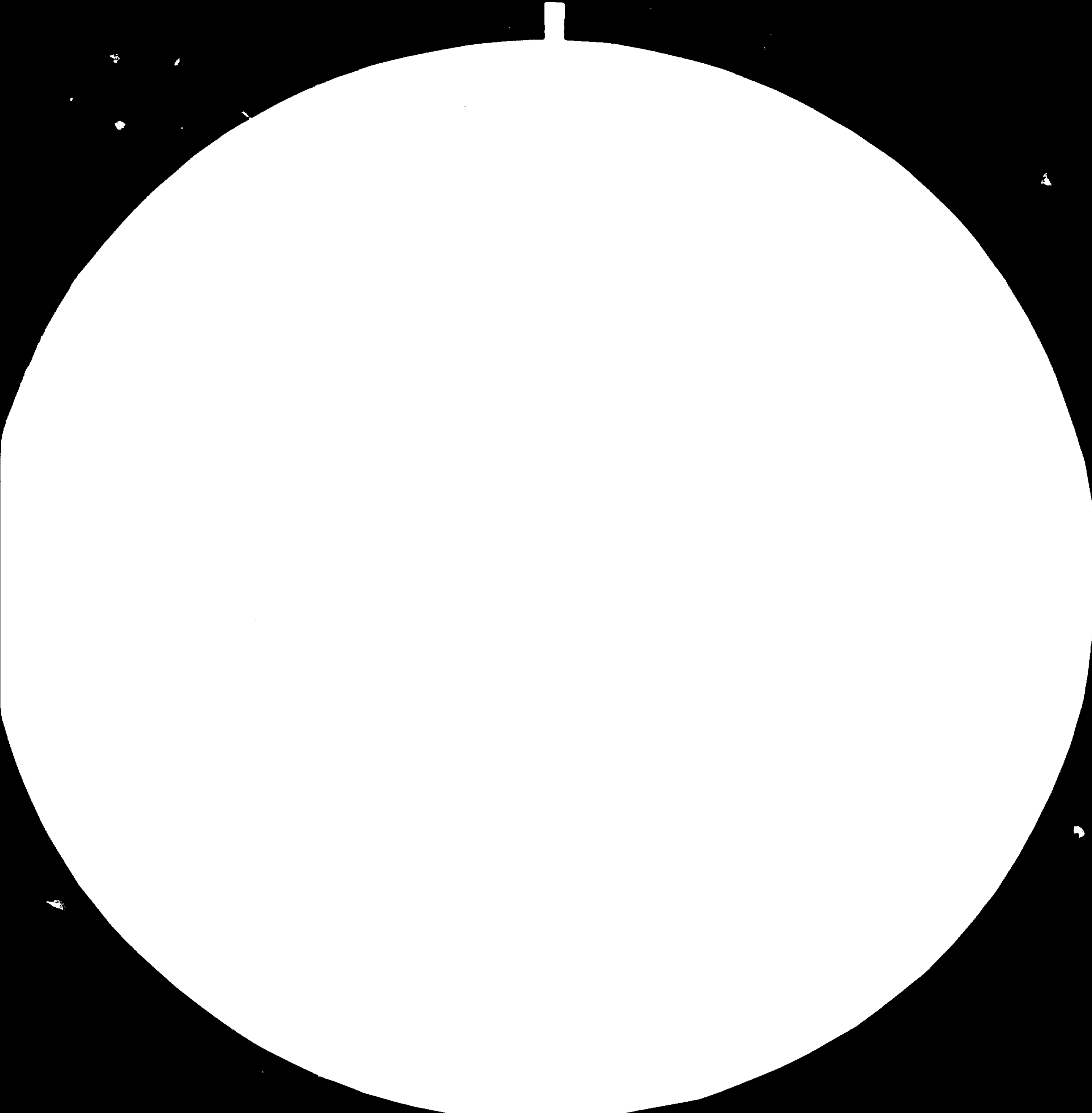
All mixes in Table 6 showed some flow marks, however, which would be accentuated in moulding a bumper due to the higher ratio of flow path length to thickness. The conclusion was reached that reduction of flow marks resulted when homopolymer PP was replaced by copolymer PP and also when MFI was increased. Probably the copolymer is more compatible than homopolymer with NR. Atactic poly(propylene), which was tried as a possible additive to increase compatibility, was ineffective.

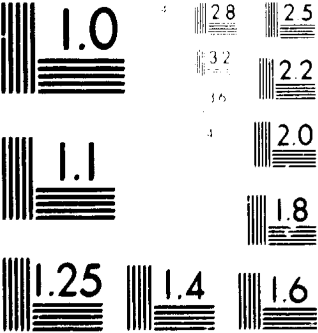
In further experiments it was found that flow marking was reduced when the amount of black was increased from 2 to about 10 parts.

Subsequently a change was made in the method of assessing the ability of a mix to be moulded without flow marks, using the Arburg. Whereas previously the machine had been operated to minimize flow marks, it was now set to make them more prevalent by increasing the injection time and reducing mould temperature. This could be a better guide to large scale moulding trials.

Table 7 shows several compounds containing plasticizers. Flow marks were virtually eliminated by raising the MFI to approximately 20. It will be noted that flexural modulus has been kept approximately constant by changing the NR/PP ratio to offset the softening effect of oil.

Petroleum jelly bloomed slightly after several days exposure to light. The high viscosity oils did not cause tackiness, as had been the case with a low viscosity oil tried previously, and samples exposed outdoors for several weeks improved in mar resistance.





MICROCOPY RESOLUTION TEST CHART

[illegible]

TABLE 7 PLASTICIZATION OF TPNR TO INCREASE MFI

SMR L	50	40		40
OENR (25% oil)			50	
PP copolymer [1]	50	60	50	60
FEF black	10	10	10	10
Petroleum jelly	5	15		
Mineral oil [2]				12
Antioxidant	0.5	0.5	0.5	0.5
MFI (230°C/5 Kg)	12	28	22	21
Flexural modulus, MPa	270	260	270	280
Surface texture	flow marks	slight flow marks		virtually no flow marks

[1] Shell's RMT 6100 (MFI = 10 with 2.16 Kg load)

[2] Sunpar 2280 and Dutrex 729 were used; both high viscosity oils.

The formulation in column 4 of Table 7 is the best so far developed. As the conditions of moulding were designed to accentuate flow marks it is considered that in normal practice it will give excellent processing. Further trials on the production of the Saab bumper are in progress.

The physical properties of the TPNR from this formulation are given in Table 8 and it can be seen that they match those of the currently used Vistaflex 911B very closely.

TABLE 8 PHYSICAL PROPERTIES OF OPTIMISED FORMULATION

		TPNR*	VISTAFLEX 911B*
MFI (230°C/5 kg), g/10 min		21	14
Flexural modulus, MPa	a	270	240
	b	190	-
Tensile stress 50% strain, MPa	a	14	12
	b	7.7	7.5
Tensile stress 100% strain, MPa	a	14	12
	b	7.6	7.5
Tensile stress at break, MPa	a	14	12
	b	8.5	8.2
Elongation at break, %	a	190	230
	b	400	540
Crescent tear, N	a	115	-
	b	70	-

* 2 mm sheets injection moulded on Arburg machine

3.2.2 Large scale production

No difficulties have been encountered in producing TPNR blends on a sizeable scale. Normally the Shaw K2A mixer has been used for a batch size of 25 kg. The usual procedure is to commence with the mixer at a temperature of about 80°C, not to have either steam-heating or water-cooling during mixing, but to use the fast rotor speed (50 rpm) and full ram pressure (100 psi). In this way the batch heats up rapidly; the temperature and power recorders indicate that melting of the poly(propylene) occurs after approximately 2 minutes. A small amount of crosslinking agent (if used) is added at $2^1/4$ minutes and mixing continued for a further 2 minutes. Antioxidant is then added and one minute later the batch is dumped, giving a total mixing time of 5-5½ minutes. The dump temperature, as measured by a thermocouple probe, should be 170°C to 190°C. With a cycle time of ca 10 minutes the rate of production is 150 kg/hour and it is therefore easily possible to prepare a tonne of TPNR in a normal working day using what is the smallest factory scale equipment.

The mixing cycle in the K2A can be a useful guide to mixing in larger machines, but it is very important to observe temperatures and power consumption as accurately as possible in order to avoid dumping at

a) too low a temperature, such that the poly(propylene) has not been adequately fluxed or

b) too high a temperature, which may cause degradation of the polymers and increase their odour.

On a larger scale a custom compounder (British Vita Ltd) has prepared TPNR 6040 (60 parts SMR L, 40 parts poly(propylene) with small quantities of carbon black, antioxidants and peroxide crosslinking agent) in a 3D Banbury. The Banbury was warm initially (having been used immediately beforehand to peptize some rubber) and the batch volume was 55.5 litres. At the end of 5½ minutes mixing the indicated rotor temperature was only about 150°C, but the batch was at 205°C, ie hotter than anticipated or desired. It was concluded that to control the batch temperature more precisely it may be necessary to use cooling water on the machine and/or to reduce the batch volume to about 50 litres. Thus TPNR can be manufactured in high speed internal mixers without the need for heating. Low speed mixers may need this facility, however.

3.2.2.1 Sheeting and granulating The batch from the internal mixer will normally be dropped onto a two-roll mill. At MRPRA the K2A batches of TPNR are sheeted on a 42 inch mill having cool rolls. It can be passed once or twice through the nip, but not more, because when the temperature drops below about 160°C there is an increasing tendency for the material to flake and crumble as it passes through the nip, making it difficult to handle. This problem was experienced with batches from a 3D Banbury being dropped onto a 60 inch mill. Each batch was too large for the mill operative to be able to take it all from the mill before the material had cooled to this critical state. However, it was judged that the problem would not have arisen if the mill rolls had been heated.

TPNR is very tough when cold. Therefore it is best to cut the sheet while it is fairly hot into pieces small enough for subsequent feeding to a granulator. However, if this is not convenient the cold material can be guillotined. Both methods have been employed at MRPRA to provide pieces about 10 inches square which are suitable for our Blackfriars granulator, model 12 ASHD, which has a throat size of 8 x 12 inches and a rotor speed of 1 500 rpm. The TPNR should be cold before being fed to the granulator. A small quantity of partitioning agent (talc or zinc stearate) is required with TPNR containing more than about 50 per cent rubber, but harder blends (less than 50 per cent rubber) give free flowing granules without a partitioner. The screen should be one with 6 to 8 mm diameter holes and with this size fitted to the MRPRA machine, a throughput of about 100 kg of TPNR 6040 per hour is obtained.

TPNR should be stored in a cool warehouse in suitable containers, for example in polythene or paper sacks containing 25 kg. There may be a tendency for softer grades of TPNR to cake under pressure, especially if insufficient partitioning agent is present. This friable cake can be fairly easily reconverted to free flowing granules by breaking it down and shaking with extra partitioning agent.

3.2.2.2 <u>Grades of NR</u> SMR [illegible] is used for natural, white and coloured grades and also for black grades that are afterwards painted, so that any possibility of the substrate contaminating the paint film is reduced. Another reason for using a high grade of NR is that odour resulting from the high temperatures employed during processing is reduced. If for economic reasons it is necessary to use a cheaper grade of NR such as SMR 10, the physical properties are not likely to be affected. Grades of PP have been discussed in 3.2.1.4.

3.2.3 Economic analysis of production costs

3.2.3.1 <u>The production unit</u> The simplest possible production unit has been chosen: an internal mixer, a sheeting-off mill and a granulator to convert the sheeted blend into material suitable for subsequent processing elsewhere, eg by injection moulding. More sophisticated configurations include the possibility of blending powdered NR with PP in a powder blender followed by extrusion.

The mixing procedure is based on current MRPRA experience with a small factory-scale mixer (25 kg batch weight). The mixing cycle required is 6 minutes. At the start of each cycle the NR and PP are added to the mixer; after about 3 minutes (by which time the PP has melted) the dicumyl peroxide (if used) is added, followed by the antioxidant. No doubt, in a production process this could be systematized and automated. It should not be necessary to provide external heat to the mixer, and use of cooling water should be small and will be neglected. At the end of the cycle the mix is dumped and immediately sheeted out on the mill, the sheets being subsequently fed into a simple granulator.

It is envisaged that such a production process would normally be set up and operated as a dedicated operation within a normal rubber goods factory, rather than in the form of intermittent use of existing equipment. Thus, in order to form a realistic estimate of capital costs it is necessary to make allowance for the full cost of utilities, buildings etc.

3.2.3.2 Processing costs As before, the assumed production unit is that based on a 75 kg batch weight internal mixer plus mill and granulator, with a theoretical hourly production rate of 750 kg. Total capital cost is £500k made up of £170k for a mixer, £80k for a mill, £40k for a granulator with dust extraction equipment, and £210k for utilities, buildings etc.

Given the high rate of inflation in equipment costs it would be prudent to assume that any organization setting up such a unit in Europe today would aim to recover the initial cost as quickly as possible, and would similarly require a fairly high rate of return on the investment. It is likely that organizations would seek to recover the initial cost in as little as five years. A rate of return of not less than 25 per cent/year would not be regarded as too high a target, bearing in mind that the current base lending rate in the UK is 17 per cent/year. This indicates an annual capital cost of just under £200 k.

The assumed production unit is to run on a two-shift basis, 16 hours/ day, 5 days/week, 48 weeks/year, with seven operatives. The theoretical output is 750 kg/hour, but it is unrealistic to assume that this maximum output could always be achieved, and it will be prudent to reduce this by 10 per cent, ie to 675 kg/hour, giving an annual production of 2 600 tonnes. Thus, the annual capital cost is £200k/2 600 per tonne, and this will be rounded up to £80/tonne.

Current UK earnings for process workers in the rubber industry (excluding the tyre industry) average about £90/week. It would be normal practice to add around 100 per cent to process workers' wages to cover other wages and salaries, insurances etc. This gives a total labour cost of £120k/year, corresponding to £50/tonne. UK wage rates in the rubber industry are low, even by UK standards, and certainly these costs would be much higher in most other Western countries.

The power requirements (electricity) are estimated to be 600 kWh/tonne. In the UK, the cost of electricity is £0.04/kWh, ie £24/tonne. To allow for a certain increase in electricity charges in the near future, this will be increased by 10 per cent, ie to £27/tonne.

Concerning maintenance, discussion with one leading custom mixer has emphasized that this has become a very costly item. As long ago as 1974 one such firm in the UK reported that they allowed £3 000/year per machine for maintenance. This figure was based on a charge of £30/day for fitters' time; since a current charge would be ca £120/day, it can be inferred that ca £12 000/year should be allowed for maintenance, corresponding to £5/tonne.

Table 9 brings together the above estimates. In round figures, processing costs in the UK are likely to be about £160/tonne. For reasons to be discussed, this must be regarded as a minimum figure.

TABLE 9 PROCESSING COSTS

	£/tonne
capital [1]	80
labour [2]	50
power	27
maintenance	5
	162

[1] includes 25 per cent/year return

[2] includes 100 per cent overheads

3.2.3.3 Custom mixing costs During the development of TPNR there has been, perhaps, a tacit assumption that this is a material which would be produced and marketed by some form of entrepreneurial organization which would thus undertake the role of a polymer producer. There are of course alternatives: (i) TPNR could be made to order by a custom mixer, either directly for a consumer or on behalf of an organization interested in undertaking marketing of TPNR, or (ii) it could be made for a major end user (eg a car manufacturer) by one of his normal component suppliers who would also fabricate the TPNR into products for the end use.

It is interesting to take note of the charges that a custom mixer is likely to make. A current quotation by the largest UK custom mixer is £215-£275/tonne for mixing (depending on scale) plus £80/tonne for granulating. Taking the lower value, the total is around £300/tonne. This is much higher than the theoretical cost of £160/tonne. Interestingly, it is in line with a 1978 US quotation for TPNR which, after making allowance for raw materials costs, is equivalent to about £220/tonne for mixing (presumably without granulation: this was not stated). Also in line is a general quotation from another UK custom mixer, that mixing of normal compounds on a 4-minute cycle costs £180-220/tonne.

It must be accepted that custom mixers' charges will generally look high in comparison with costs evaluated for a regular, fairly large-scale operation. Custom mixers are providing a special type of service (eg helping out a manufacturer who has a temporary shortage of mixing capacity, an emergency, or the need for a non-standard mix in smallish quantities) and they charge accordingly. The organization whose charges are cited above described their operations as 'very profitable'.

If the object is to keep processing costs for TPNR as low as possible, then the inference is that production by a custom mixer is not the best choice unless one can interest a custom mixer in the idea of regularly producing TPNR on a large scale (in this case he is no longer fulfilling the role of a 'custom' mixer but has become a polymer producer). Possibly one might then get the cost down to a more acceptable level.

3.2.3.4 Material costs These are obviously dependent on the formulation used for TPNR. As one particular formulation has been discussed earlier as giving optimum processing properties for the injection moulding of large automotive components this will be made the basis of comparison with its synthetic rival. The formulation and material prices are set out in Table 10.

TABLE 10 MATERIAL COSTS FOR TPNR

Material	Cost (p/kg)	Weight used (kg)	Total cost (£)	
SMR L	66.5*	40	26.6	
PP copolymer	61.5	60	36.9	
FEF black	36	10	3.6	
Oil, Sunpar 2280	35	12	4.2	
Flectol H	200	0.5	1.0	
		122.5	72.3	= £590/tonne

* includes part handling charges and delivery to factory

3.2.3.5 Total costs We have a total raw material cost of £590/tonne. The amount to be added to this for processing depends on circumstances. In the case of a large dedicated plant (eg one that is operated by or on behalf of a major end user) there is no reason why these costs should greatly exceed the figure of £160/tonne. In such a case there are no marketing costs. In situations where the TPNR is being produced for external sale then some allowance must be made for marketing, perhaps 2 per cent of sales, leading to a total cost (without raw materials) around £180/tonne.

Adding these costs together leads to the conclusion that the minimum price at which one could expect profitably to produce TPNR in the UK for external sale is about £770/tonne. For intra-company sales the price could be a little less. On the other hand, should it prove necessary to go to a custom mixer and to pay the full commercial price, then the TPNR price rises to £890/tonne. This, it may be supposed, would be appropriate only if one requires to establish a basic production facility in order to test the market.

The current UK selling price for all-synthetic TPR (ISR's Unipren Type 720) is £1 070-£1 130/tonne depending on quantity. That of Vistaflex 911B, which is currently used for production of the Saab bumper, is £975/tonne. Thus, TPNR has a useful advantage in price of ca £100-200 according to its provenance.

3.2.3.6 Costs of production in a developing country Material costs in an NR producing country in Asia are likely to be similar to those in Europe. The lower cost of NR which does not have to bear freight charges or export duties will be offset by higher costs for imported PP and chemicals.

While machinery and factory costs will be roughly the same as in Europe the capital cost per tonne will be lowered to ca £40 because of the lower rate of return required (pay-back over 10 years at 15%/year return on investment). Power and maintenance costs will be similar but labour costs/tonne will be substantially reduced from £50 to £5 by the much lower wage rates in Asia. Thus the production of TPNR in, for example, Malaysia will cost at least £80/tonne less than in Europe while imported synthetic TPR's will be more expensive than in Europe because of freight charges/duties. There must be an excellent case for the setting up of production facilities for TPNR to supply the expanding local rubber products manufacturing industry. Production of TPNR for export would also be possible although part of the price advantage would be lost in transport costs (say £50/tonne to Europe).

3.2.4 Applications and promotion of TPNR

The physical and processing properties of TPNR and the economics of its production have been developed to be similar or better than synthetic TPR's already in commercial use. A major effort was therefore necessary and justified for the identification of suitable applications and the promotion of TPNR to potential users via sampling and collaborative trials. The major areas covered are listed below:-

Automotive components This area was considered to hold great potential for TPNR and has therefore received special attention.

The most important single application is in rigid, impact resisting car bumpers. Two trials have been carried out with Skandia Fabriken in Sweden who currently injection mould Saab bumpers using Vistaflex 911B. The first involved the supply of 400 kg of a TPNR 6040 formulation containing a peroxide crosslinking agent. This met the Saab specification for physical properties but bumpers moulded on the Demag 1250 tonne machine had an unsatisfactory surface appearance (see Figure 4). The bumper mould has a long flow path and a thin section making melt flow viscosity a critical factor.

A second trial used a TPNR 5644 formulation based on a PP copolymer (Shell KMT 6100) and no crosslinking agent to give a higher MFI of 3.6. Mouldings were considerably improved but still not good enough. A third trial is to be carried out using the optimised formulation discussed earlier and containing processing oil to give a high MFI of 21. From the results of injection moulding this material on the Arburg machine under difficult conditions it is expected that satisfactory mouldings of the bumper will now be obtained.

Trials for the injection moulding of car bumpers from TPNR are also being undertaken by CPIO (France), Saga (Norway) and Rolinx (UK).

Other automotive components for which collaborative work has been carried out include car mats (Itailastik, Italy; odour a problem), car radio speaker gaskets (approved by Chrysler, USA but no supplier of TPNR as yet in the USA) and vacuum-formed sheets as sound deadening panels (Revertex, UK, work still proceeding).

<u>General applications</u> British Vita are currently investigating the use of TPNR as a lining for tanks in chemical plants. They are making their own TPNR and have shown that chemical resistance and adhesion is good.

Ferodo (UK) have been carrying out collaborative trials with TPNR (based on both PP and poly(ethylene)) for extruded stair nosings. They are now mixing their own TPNR for larger scale trials.

Several applications in footwear have been investigated. Partizanske, CSSR, are looking at TPNR blends in this respect as are Weber and Schaer, FGR (properties satisfactory for shoe soling but odour a problem), Bata, Malaysia (satisfactory for injection moulded sole units) and CTC Industries, Italy (trials in progress on ski boot applications).

TPNR 4060 rail pads moulded by Birger Berg are performing well in service trials carried out by the Norwegian State Railways.

Products made by extrusion processes have been included in the applicational trials. Dunlop (Angus) have made a fabric-reinforced irrigation hose from an oil extended TPNR blend but the fabric adhesion was poor. The extrusion of garden hose was satisfactory. Bofa Kabel, Sweden and BICC, UK, are carrying out trials on the extrusion of cable coverings. Initially rough extrudates were obtained but blends with improved processability have been satisfactory.

Miscelleneous applications include transponder boxes moulded by Fullwood Bland, UK (now on service trial); replacement for nylon and PP bin handles (Capper Injection Mouldings); hard containers/buckets (Wm. Freeman, UK, Figure 5); babies chew rings (Cannon Rubber, UK); gaskets (Rostero, UK) and underground pipe joints/connectors (Ketch Plastics, UK). Small quantities of TPNR blends have also been supplied to a variety of companies for evaluation in the manufacture of roller skate wheels, electric plugs, wheel trims, battery components and assorted household goods.

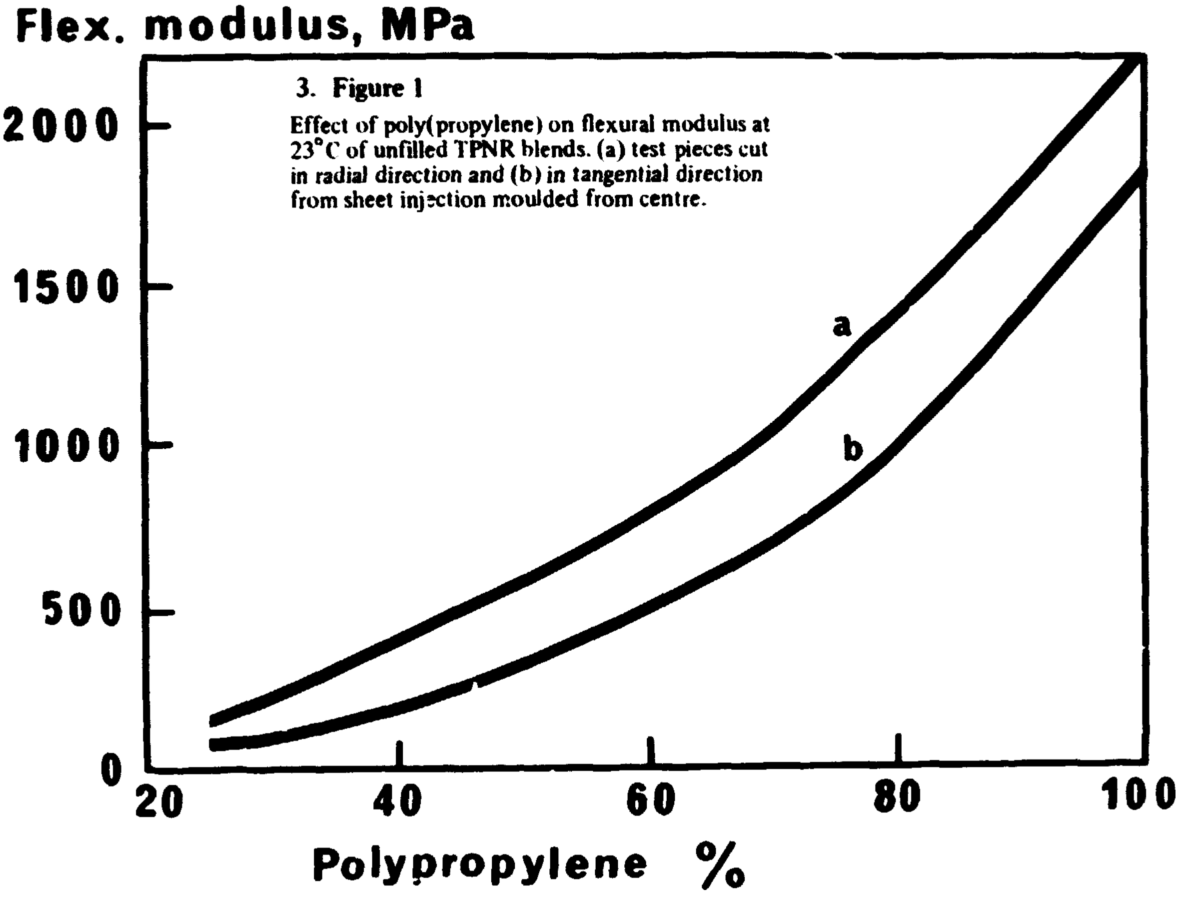
In summary, a wide range of potential applications for TPNR blends have been examined in the course of promotion of the material to potential commercial users. Although no large scale uptake has yet materialised the generally satisfactory performance of TPNR in service trials and its attractive pricing should mean that this will occur as the inertia of industry is overcome.

3.2.5 Problems remaining

The technical problems remaining are very minor except for that of odour. At the high mixing and processing temperatures used the non-rubbers in NR give rise to a typical 'burnt' odour which has been found to be objectionable in certain applications.

The odour can be minimised by careful temperature control during mixing and processing and this seems to be the best approach. Re-odorants to mask the unpleasant odour with one, say, of leather are also useful.

Further attention will need to be given to blending in continuous mixer-extruders which may lessen the odour problem by milder conditions of mixing. Pelletisation by extrusion/chopping must also be explored as industry prefers more regular particles than obtained by granulation methods.

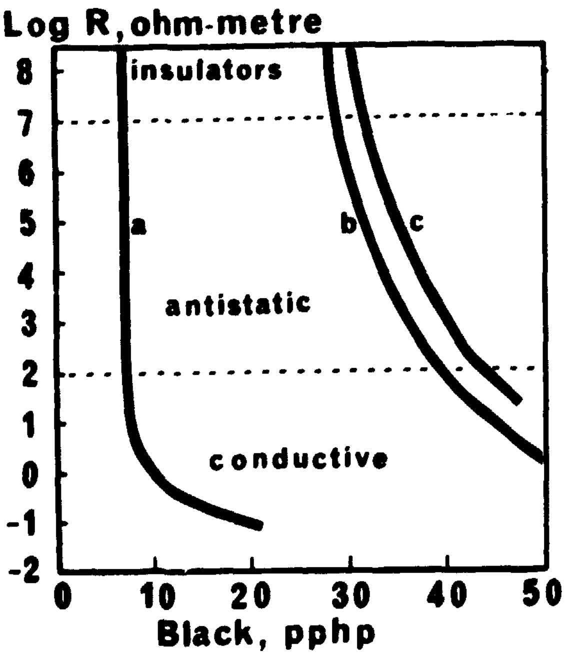


3. **Figure 1**

Effect of poly(propylene) on flexural modulus at 23°C of unfilled TPNR blends. (a) test pieces cut in radial direction and (b) in tangential direction from sheet injection moulded from centre.

3. **Figure 2**

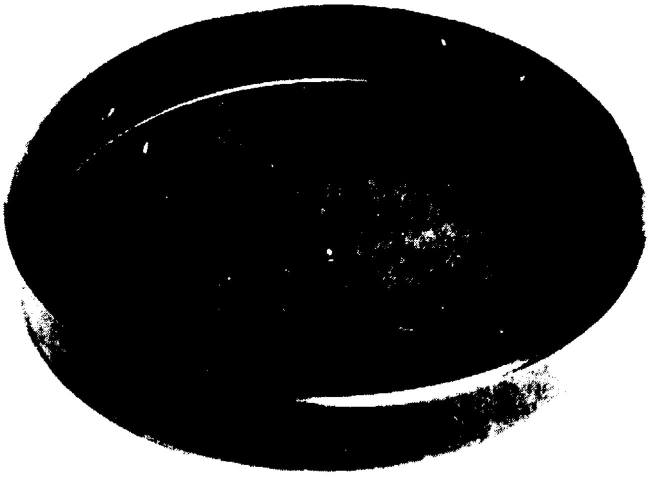
Effects of exposure to 50 pphm ozone at 40°C for 7 days, 20% surface strain on (left to right) vulcanized NR: TPNR 4060; TPNR 5050; TPNR 6040. All samples contain HAF black but no antiozonant.



3. **Figure 3**

Effect of carbon black on volume resistivity of TPNR 6040. (a) Ketjenblack EC (b) Vulcan XC72-N472 and (c) Vulcan 3H-N347.

3. **Figure 4** SAAB bumper cover moulded from TPNR 6040.



3. **Figure 5** Pipe end closure (200 mm diameter moulded from TPNR 1585 containing 1% carbon black.

4 POWDERED NATURAL RUBBER

4.1 INTRODUCTION

There have been many assertions as to the future potential of powdered rubbers as energy and cost saving materials ideally suited for the automated factories of the future. However, when the project started there were still many unanswered questions on the behaviour of powdered rubber versus bale rubber in transport, storage and processing and on the economics, specifically whether the extra cost of producing a powdered rubber could be recovered in savings made through its use.

This was especially so for natural rubber where there was little knowledge or expertise in the production or use of powdered NR. For NR there is only one commercial manufacturer in an NR producing country (Malaysia), who obtains a fine powder by spray-drying latex, the use of which is limited mainly to the preparation of rubber solutions for adhesives (fast dissolution); output is a few hundred tonnes/year, probably only 10 per cent of plant capacity. Other than that, the only NR used in powder/granule form is that which is custom-granulated from bales in consuming countries, either in-house or by companies which specialize in this; the quantity involved is much less than 1 per cent of NR consumption.

The project was designed to fill this information gap so that the NR producing countries and users of NR could see and take advantage of any large future potential for a powdered form. In this Report the term 'powder' is arbitrarily used to describe a free-flowing form of NR ranging in particle size from less than 1 mm to 12 mm diameter.

4.1.1 Concept

Three main elements to the project were envisaged:-

(i) The study of existing and new methods of production of powdered NR and of the transport and storage stability of the different types.

(ii) The comparison of processing characteristics and product properties of powdered NR of different type, particle size and partitioning agent with those of bale rubber using both conventional and powder-orientated processing machinery.

(iii) The examination of the economics of production and use of powdered NR.

4.1.2 Implementation

Several production routes have been investigated of which the most promising on economic and technological grounds are brominated crumb NR and mechanically-granulated NR. The former process was invented during the course of the project to meet the requirement that NR producers should be able to make free-flowing NR directly and cheaply from latex.

Whatever process is used it is necessary to prevent re-agglomeration of particles during production and transport. Normally this is done by incorporating a 'partitioning agent', typically talc or silica. An alternative approach is chemically to treat the surface of the NR particles in some way so as to make them less tacky. As far as is known, this has not previously been tried and the method devised for the project is novel. It involves treatment with bromine water, and preliminary experiments showed that the procedure was feasible. Subsequently a pilot plant was set up at the RRIM in Malaysia. The granules produced travel well with little re-agglomeration and the material processes adequately, but the overall cost of the process is higher than that of mechanical granulation (especially since it was later found necessary to use longer-than-expected drying times).

Mechanical granulation is not novel but its simple practicality suggested that experience in its use needed to be gained and it provides a convenient means for examining variables such as particle size and partitioning agent and for producing bulk quantities for large scale processing trials, using the standard commercial granulator installed as part of the project equipment. Much useful data has been obtained on features such as optimum particle size, throughput under various conditions, choice of partitioning agent, and so on.

Using mechanically granulated, brominated crumb and spray-dried latex, trials of processing performance have been carried out in conventional internal mixers and in two of the newly-available powder processing machines: 'mixer-extruders' equipped with vacuum venting to remove entrapped air and volatile substances. Such machines can accept material from a powder blender and produce a precision extrudate ready for vulcanization. During the trials, particular attention was paid to energy usage in view of claims made on this point: with the internal mixer there is some small saving of energy (4-12 per cent) and there is also some saving with the mixer-extruders, though this seems to be associated with high extrudate viscosity and poor dispersion, and production of better-quality extrudates may eliminate the energy saving. A trial was also carried out on the direct injection moulding of granulated NR, using a machine devised specifically for this; the results were only moderately satisfactory.

Sufficient experience has been gained in formulating mixes for various situations to be reasonably confident that the procedures needed are well understood. In fact, devising formulations for powdered rubber processing involves nothing more than the intelligent application of standard rubber technology, eg attention to features such as 'scorch safety', although it has to be recognised that processing conditions in mixer-extruders are less flexible than in conventional machinery.

Estimates have been made of the likely cost of production by various processes in Malaysia, and by mechanical granulation in the UK. The cheapest of the three Malaysian processes assessed is 'talced crumb', made simply by adding talc to NR during its comminution in the normal block rubber process (a process formerly operated on a modest commercial scale). The factory cost, extra to that of the starting NR, is low (£27/tonne) but unfortunately the material is not commercially viable because its storage life (re-agglomeration) is too short for export and probably for domestic use. Spray-dried latex is the most expensive (£124/tonne) and the new brominated crumb process was originally costed at £72/tonne but this must now be increased to allow for extra drying time. For all three forms, since their density is about one-half of that of bale NR, and since freight is charged on a volume basis, there is a substantial extra cost for ocean and land freight, plus insurance, assessed at about £70/tonne. Thus, there is no viable technology at present capable of landing powdered NR in a consuming country at a premium over bale NR much less than about £150/tonne which is too high. Brominated crumb, though, is a possible candidate for domestic use in NR producing countries. For mechanical granulation in a consuming country the extra cost is calculated at around £100 for granulation in a custom-built factory. This is in line with commercial prices in the UK. For granulation in a user's factory the cost will be lower by up to £40/tonne because of reduced packaging, working capital, administration and other overhead charges, depending on individual circumstances and arrangements.

Estimates have been made of <u>total</u> production costs of (a) unvulcanized strip and (b) a continuously vulcanized finished extrusion in a new factory equipped with conventional Banbury mixers using bale rubber or with MVX mixer-extruders using mechanically comminuted rubber at a premium of £100/tonne. This suggests for (a) a cost disadvantage for the powdered route of £15-£80/tonne of product depending on the assumptions made of MVX output. For (b) [illegible] disadvantage of £16/tonne under likely output conditions could become a similar sized cost advantage with the most optimistic output assumptions. The cheaper 'in house' cost of granulation mentioned above will affect the picture but it is clear that at the present stage the processing savings of the powder route do not normally offset the premium charged for the powdered NR. As the processing machinery develops with higher outputs relative to capital charges/labour costs then the use of powdered rubber may become more attractive.

4.1.3 Outcome

Several routes (spray-dried latex, brominated crumb rubber, mechanically ground rubber) are available for the large scale production of powdered NR if consumers require this. All types process easily on conventional mixing equipment to give products which are fully equal to those from bale rubber. However there is no overall technical or economic advantage.

The use of continuous mixer-extruders designed for powdered rubbers did show process cost savings which under the best circumstances recouped the premium on the cheapest form of powdered NR, ie in-house mechanically ground. The properties of products so derived were adequate for general purpose use but not for the more demanding applications. Overall, the impression gained is that a good deal of work will need to be done by machinery manufacturers before the processing of powdered rubber on the new machines will approach the predictability and versatility of conventional processing of bale rubber and result in sufficient savings to justify the premium incurred on the raw material.

It has not yet proved possible to devise a form of powdered NR which is economically viable for export from NR producing countries. Given the small processing cost advantage that a consumer will see (which will be reflected in the premium he is prepared to pay) and given the high extra cost of freight, attainment of this objective will be very hard. For use in NR producing countries this part of the project has yielded some valuable leads. Brominated crumb is a candidate for domestic use, and it is also possible that some of the information on mechanical granulation could be adapted for the conditions in NR producing countries (where clearly it would not make sense to produce NR in bales for subsequent granulation). As the rubber manufacturing industry expands in the producing countries the design of new factories around powdered rubber processes may well be advantageous for certain products.

4.1.4 Problems relevant to further implementation

Assuming that the main objective ultimately is to devise an exportable form of powdered NR the main problem is that of the high extra freight associated with low-density powder or granules. What is needed is a way of temporarily aggregating NR particles in such a way that their density for transport is greatly increased; subsequent easy dis-aggregation in the consumer's factory will be essential.

The other problem is one for the rubber machinery manufacturers, - the provision of processing equipment which will realise the potential savings in costs, energy and the facilitation of automation in the rubber factory through the use of powdered rubber.

4.2 BODY OF REPORT (POWDERED NR)

4.2.1 Processes for production of powdered NR

Three different types of powdered/granulated NR have been investigated in detail during the project:- spray dried latex (Crusoe rubber), mechanically ground rubber and brominated crumb rubber. The processes by which these are made are described below.

4.2.1.1 Spray dried latex In the production process for spray dried powder rubber, field latex is blended in bulking tanks at the factory in order to produce a consistent rubber. The blended latex is then creamed with Alginate to raise the dry rubber content of the latex from 30 per cent to approximately 55 per cent: this process takes 8 hours. To stabilise the Mooney viscosity of the natural rubber, hydroxylamine neutral sulphate is added to the creamed latex and dispersed thoroughly.

In order to maintain the free flowing characteristics of powdered natural rubber it is necessary to use a partitioning agent. The partitioning agent used raises the viscosity of the powdered rubber by 5-7 Mooney points. To meet the specification of 70± 5 Mooney it is therefore necessary to choose latices of no higher than 60± 5 Mooney viscosity.

The creamed latex is pumped from a feeder tank up to the top of the spraying chamber from where it is fed into the spray chamber. As the latex enters the chamber it comes into contact with a high speed disc which atomises the latex. At the same time hot air at 190° to 200°C carrying the partitioning agent is introduced into the chamber; this hot air flash dries the latex particles which are immediately coated with the partitioning agent. The coated particles of dried rubber then fall to the bottom of the chamber from where they are taken through a rotary cooler. The powdered rubber containing approximately 6-8 per cent partitioning agent is packed into 20 kilo paper bags. Excess partitioning agent and very fine particle rubber is removed by the cyclone and collected in bag filters.

The choice of partitioning agent has proved to be very critical in obtaining the best possible particle coverage whilst retaining a minimum of non-rubber constituents in the rubber. From extensive trials it has been found that a very fine particle size partitioning agent is necessary to optimise these two factors. It has also been necessary to avoid partitioning agents which are hydrophilic, as the presence of water around the rubber particle tends to cause agglomeration of the rubber. The third aspect related to the use of the partitioning agent is the need to use a material that does not detrimentally affect the quality of the rubber. The most effective type of partitioning agent found to date to fit all these requirements is a reinforcing grade of silica.

The packaging is important to the quality of the delivered material. It has been found that when Crusoe rubber is packed in polythene bags, moisture contained within the rubber cannot escape and this encourages agglomeration. However, if the rubber is packed in paper bags moisture is allowed to escape and the storage stability (free flowing properties) of the powder is greatly improved. The temperature of packing is also very important. Rotary coolers have been installed to reduce the temperature of the powder to a maximum temperature of 15°C before packing.

The product is very fine, more than 60 per cent will pass through a 2 mm sieve.

Crusoe rubber packed in 20 kg paper bags has been stored inside a warehouse in ½ tonne pallets for one year after being shipped from Malaysia to the United Kingdom. At the end of this period the material was, although compacted, still very friable and useable as a free flowing powder.

4.2.1.2 Brominated crumb rubber In one sense this material is derived from latex as it makes use of the wet coagulum after acidification of latex but it does not utilise the original particulate structure.

To latex is added 0.5% of a mixture of castor oil and zinc stearate (in the ratio of 6:1) and the latex is coagulated with formic acid. (For the preparation of viscosity stabilized, free-flowing crumbs, 0.15% hydroxylamine neutral sulphate is added to the latex before coagulation). The coagulum is first passed once through a creper with diamond shaped grooves on the rolls. Clusters of large crumbs are obtained, which are then fed twice into a smooth-roll creper, whose gap between the rolls is adjusted to between 0.10 and 0.15 mm. This gives smaller and more discrete crumbs. A further quantity of zinc stearate (1%) is added, and the crumbs passed three more times through the creper. The coagulum is completely converted to discrete, compact crumbs. These crumbs remained discrete when mechanically stirred in water thus allowing homogeneous reactions on the surface of the crumbs to be carried out.

Bromine is generated by the addition of 20% w/w sulphuric acid to an aqueous solution of sodium bromide and sodium bromate. The acidic solution of bromine of known concentration (0.13 mole/l) is then added to the dispersion of crumbs in water. The extent of bromination is controlled by limiting the quantity of available bromine to 0.86% w/w on dry rubber. The reaction between the crumbs and the bromine progresses to completion very rapidly. The brominated crumbs are then well washed and dried in hot air.

The rubber obtained is in the form of irregular-shaped, discrete, free-flowing crumbs. Batches of approximately 200 g of the crumbs were run through a series of British Standard testing sieves for 20 minutes on an Endecott sieve shaker. The particle size distribution is given in Table 1, 98% by weight of the crumbs are in the 1-10 mm size range.

TABLE 1 PARTICLE SIZE DISTRIBUTION

Particle size	% by weight	
	as prepared	after breaking-up friable bale
4 mm - 10 mm	20	6
2 mm - 4 mm	61	72
<2 mm	19[(a)]	22

(a) consists of 17% between 2 mm and 1 mm and 2% between 0.5 mm and 1 mm

Batches of approximately 1 kg of the free-flowing crumbs were compressed in a 23.4 cm x 10.7 cm section mould under a 40 kg load (160 g/cm^2) for 48 hours at ambient temperature to produce mini bales. The compacted bales had a packing density between 0.70 and 0.75 g/cm^3 (compared to density of bales of SMR between 0.8-0.9 g/cm^3). They were wrapped with polythene sheets and stored at ambient temperature (21°C).

After 30 days, all the mini bales were found to be friable, ie they could be easily crumbled to return to a particulate form again. In one trial, the mini bales were divided into pieces of about 100 g each and loaded into a powder blender operating under various conditions. The compacted bales were found to disperse completely into free-flowing crumbs in 3 minutes at 3 500 rpm. Table 1 shows that 14% of the largest size range, 4-10 mm, had been disintegrated into smaller particles. This indicates that as prepared, this portion of the crumbs in the 4-10 mm size range consists of loosely-linked clusters of small crumbs.

Analytical, raw rubber and vulcanizate properties were discussed in detail in the First Progress Report (3.4.3) and the Second Progress Report (3.3.1, 3.3.2).

A pilot plant for the production of free-flowing brominated natural rubber crumb has been set up in the Rubber Research Institute Experimental Station in Malaysia. The target output of the plant is 0.25 tonne per shift.

The layout of the plant is given in Figure 1. The field latex is coagulated in the separate sheet coagulating tank in the form of 2 inches thick slabs. The slabs are sliced by the coagulum slicer into strips of coagulum, each with cross-sectional area of 2 x 3 inches. These strips are directly and conveniently fed into the inlet of the pelletiser. The discrete crumbs from the output of the pelletiser are transferred along the vibrating screen into the bromination tank. The brominated crumbs are scooped up by the bucket conveyor and dropped into the washing tank. After washing, the crumbs are pumped out through a static screen into the stainless steel, two-tier boxes for drying. The dryer has a capacity of 0.25 tonne per batch.

4.2.1.3 Mechanically granulated rubber There are several companies who granulate bale rubber on a commercial scale using a variety of equipment. Obviously this is a process which can be carried out in NR consuming or producing countries but it is not sensible for the latter to make bale rubber from latex and then to granulate for export with the extra freight charges this would incur.

As a typical example of the mechanical process, granulation experiments have been carried out at MRPRA with a Blackfriars Engineering Co., Granulator Model 12 ASHD which has a steel rotor with three rotating knives which cut with scissor action against two fixed knives in the steel casing. The drive motor (18.75 kW) turns the rotor at 1 500 rev/min. The knives are set as close as possible eg close enough to cut paper about 0.05-0.1 mm thick. It was known that maximum cooling would be desirable and the machine was purchased with facilities for passing cold water through the rotor and the casing. A cold draught of air assists cooling and transports rubber granules pneumatically from below the cutting chamber to the top of a cyclone which separates rubber from partitioning agent (talc).

Overfeeding becomes more frequent as the screen size is reduced and output rates are reduced as shown in Table 2. Use of talc increases but bulk densities remain the same.

TABLE 2 EFFECT OF SCREEN SIZE ON GRANULE PRODUCTION

Screen size, mm	19.1	15.9	9.5	7.9	6.4	4.8
Overall output, kg/h	30.9	19.3	15.1	14.4	12.0	6.6
Output excluding over-run time to clear chamber, kg/h	34.3	20.5	20.1	15.9	14.1	8.0
Talc used, %	2.69	4.73	2.37	3.00	3.84	6.12
Bulk density, Mg/m^3	0.43	0.44	0.43	0.42	0.43	0.44

Sieve analysis as in Figure 2 shows that particle size distribution depends on screen size and that the Blackfriars granulator can conveniently give NR particles in the range of about 4-16 mm. Particles as small as 2 mm diameter could be obtained by sieving the particles from a 4.8 mm (3/16 in) screen.

The smaller the particle size the higher the talc level tends to be as shown in Figure 3. However, particle size and talc content had little effect on raw rubber, processing or vulcanizate properties as can be seen from Table 3 which gives typical results using the K2A internal mixer for processing.

TABLE 3 EFFECTS OF PARTICLE SIZE AND TALC LEVEL ON PROCESSING, UNCURED RUBBER AND VULCANIZED RUBBER PROPERTIES

Particle (screen) size[1], mm	Bale	19.1	15.9	9.5	7.9	6.4	4.8
Talc by ash analysis[2], %	-	1.05	1.51	1.21	1.60	2.36	3.16
SMR CV 60[3], parts	100	101.06	101.53	101.22	101.63	102.42	103.26
K2A mixer							
Dump Temperature[4], °C	114	105	110	115	115	115	115
Peak power, kW	149	103	97	91	90	94	98
Specific energy, kWh/litre	0.178	0.171	0.164	0.161	0.164	0.163	0.156
Uncured rubber properties							
ML 1+4, 120°C	69	68	66	64	64	62	63
MS t_5, 120°C, min	28.5	33	33	30.5	31	32.5	32
$M_{HR}-M_L$, 160°C	24.4	24.7	24.6	25.4	25.0	25.0	25.1
Cabot black dispersion	G,H,1-4	H1-4	G1-3	H1-3	H1-4	H1-5	H1-4
Vulcanizate properties[5]							
Moulding weight, g	147.1	147.8	148.0	148.1	147.8	148.7	149.8
Density, Mg/m^3	1.140	1.149	1.145	1.146	1.145	1.150	1.158
Hardness, IRHD	66	66.5	67.5	67.5	66.5	66.5	66.5
Tensile strength[6], MPa	24.5	24.1	24.5	24.9	24.8	23.7	23.9
Elongation at break[6], %	539	535	538	537	551	538	533
M_{300}[6], MPa	10.6	10.9	10.7	11.0	10.5	10.5	10.6
Cabot black dispersion	F1-4	E1-3	F1-3	F1-4	G1-3	G1-3	G1-3

Notes. (1) As in Figure 2. (2) Analysis of natural distribution of particle sizes. (3) Rubber plus talc to give 100 parts rubber; other mix ingredients: Dutrex 729 oil, 13; Zinc oxide, 5; Stearic acid, 2; Nonox ZA, 2; N-330 HAF black, 56.5; CBS, 0.63; Sulphur, 2.6; Santogard PVI, 0.6; (4) By thermocouple probe in dumped mix. (5) Injection moulded, REP B43 K machine, optimum modulus cure 2.5-3 min, 180°C. (6) Mean of property values along and at 90° to radial mould flow lines.

Twelve common white fillers and dusting agents have been examined to see whether a replacement for talc could be found in case its use should be deprecated on health grounds. It was also of interest to see whether variations in the partitioning agent would reveal a 'best' agent or would provide further clues on the mechanism of the granulation process.

Test sieving of the granulated rubber products showed that, apart from cases of early re-agglomeration with fine silica (Hi-Sil 233) the pattern of particle size distribution is much the same for all the partitioning agents examined.

Samples having a natural distribution of particle sizes, and fractionated samples having a limited range of particle sizes, have been chemically analysed. The partitioning agents themselves have also been 'ashed' by the same technique. Ash analysis data has been corrected for natural ash in the CV rubber used and the weight losses due to ashing the partitioning agents.

It is now possible to tabulate the overall output data for the Blackfriars granulator and link it with the amount of partitioning agent that needs to be used for the granulating process and also the amount of partitioning agent which remains attached to the rubber particle after being separated from excess agent by the cyclone (Table 4).

Considering the overall output, talc is probably the best partitioning agent but it is only marginally better than zinc oxide, Hexafil clay and uncoated calcium carbonate which are therefore possible alternatives. Talc is also one of the best agents because it can be used in the least quantity. Significantly more zinc oxide (62% more), Hexafil clay (46% more) and calcium carbonate (15% more) need to be used.

Although excess quantities of partitioning agents can be collected and re-used, talc is also economical in that only about 3.75 times more talc is used than actually sticks to the rubber. Zinc oxide is efficiently used in that 1.62 times more needs to be used than finally sticks. 3.93 times more Hexafil clay and 2.4 times more calcium carbonate are needed than finally sticks to the rubber. By contrast 9.2 times more silica (KS300) or 16.4 times more Hi-Sil 233 are needed than stick to the rubber. The implication is that fine silica just flows through the machinery and into the dust collector without sticking to the rubber.

TABLE 4 BLACKFRIARS ROTARY CUTTER OUTPUT AND PARTITIONING AGENT REQUIREMENTS

	Overall output	Output excluding over-run time	Partitioning agent:-		
			used for granulation	found in granulate[3]	
Partitioning agent	kg/h	kg/h	%	w/w %	v/v %
Talc	21.8	25.3	4.84	1.29	0.52
Zinc oxide	21.5	25.44	7.84	4.84	0.94
Hexafil clay	20.6	24.9	7.07	1.80	0.75
Ppt. Calcium Carbonate[1] (uncoated)	19.93	23.42	5.56	2.30	0.96
Stockalite clay	19.7	22.6	7.60	1.47	0.61
Silica (KS300)	19.3	22.3	8.26	0.90	0.48
Ppt. Calcium Carbonate[2] (coated)	19.27	23.2	6.93	2.50	1.04
Calcium silicate	19.26	23.56	6.16	0.80	0.41
Aluminium silicate (Ultrasil AS7)	18.2	20.3	9.35	1.17	0.49
Zinc stearate	18.14	22.17	5.62	1.41	1.46
Calcium carbonate (Whiting)	16.6	19.3	11.09	2.50	1.01
Silica (Hi-Sil 233)	10.6	11.7	14.3	0.87	0.48

1 Calofort U

2 Calofort S

3 Data presented for samples having a natural distribution of particle sizes using a 7.9 mm (5/16 in) screen.

The percentage of talc by weight adhering to the rubber after passing through the cyclone is 1.29% which is significantly less than that for other relatively good partitioning agents. Less silica, less calcium silicate and less aluminium silicate than talc sticks to the rubber but these partitioning agents are not as good as talc on grounds of both output and re-agglomeration.

If carbon black could be used as a partitioning agent it should help to preserve the physical properties that are lowered by the presence of too much talc. When MT carbon black was used the cyclone worked very well and little black escaped into the atmosphere. However, it appeared that the black interfered with the efficient operation of the granulator as output was drastically reduced. Regal 300, N-326, black gave similar results.

4.2.2 Processing of powdered NR

The options for the processing of powdered rubbers are illustrated in Figure 4.

The powder process could start with powdered rubber purchased from a supplier, or bale rubber could be granulated and ground 'in house' by the rubber manufacturer. The powdered rubber is then loosely mixed in a powder blender with all the mix ingredients including sulphur and accelerators. This results in a loose powder blend which has then to be compacted and thoroughly mixed in further high shear rate processes.

Trials with powdered rubber in internal mixers have shown that some savings in processing time and energy can be made. These savings are considerable when a multi-stage process can be reduced to a single-stage process. Greater savings are claimed to be made by using a powder blender to supply a powder mix direct to an extruder or injection moulder.

Unfortunately existing conventional extruders have not the capacity to mix and extrude a powder blend with a good carbon black dispersion. A new generation of mixer-extruders has had to be developed in the last three or four years. The Farrel Bridge MVX and the Werner and Pfleiderer EVK machines are probably the most successful of these. Essential features of these machines are relatively low mixing temperatures, a means of compacting the powdered rubber, and the use of a vacuum to withdraw air and volatile materials such as water which would normally evaporate off at higher mixing temperatures in the internal mixer.

The Farrel Bridge MVX machine (Figure 5) has an air operated reciprocating ram to prevent powder from bridging and to help feed the mixing chamber under pressure. The vacuum vented mixing chamber consists of two delta rotors situated transversely above the relatively short (4-5D; D=screw diameter) extruder.

The Werner and Pfleiderer EVK machine (Figure 6) has a twin screw compacting and feed arrangement leading to a long (24.5D) vented extruder. The mixing mechanism relies on a long extruder screw with a number of shear dams which create intensive shear and which permit flow into neighbouring flight channels.

Direct shaping of hose products and direct covering of tyre bead wires with mixes having a Mooney viscosity up to 120 has been demonstrated by Farrel Bridge. If these or other extrusion products could be passed to a continuous curing process by the LCM or microwave methods the overall technique should offer useful savings. However, at present it is more common for strip or diced product from a mixer-extruder to be fed to a conventional extruder, injection moulding machine or, via mould blanking machinery, to compression presses.

4.2.2.1 Use of conventional internal mixers Very many trials have been carried out comparing the mixing of the three forms of powdered NR (spray-dried latex, brominated crumbs and mechanically granulated) in various internal mixers with the mixing of bale rubber. It is not possible to illustrate all the results but these clearly are not unfavourable for the powdered NR in terms of ease of mixing, filler dispersions achieved and the physical properties of the vulcanizates. Table 3 gives typical results for the mixing of mechanically granulated NR of varying particle size in the K2A internal mixer (25 kg batch size) using a single stage, 3 minute upside-down mixing cycle. Mixes were based on 100 parts SMR CV 60 adjusted for the talc found by analysis. Dump temperatures were not affected by the granular form of the rubber but savings of between 4-12% of the mixing energy of bale rubber were found. Wattmeter plots showed that this was mainly due to the lowering of peak power loads as the ram is put down. The financial savings may well be greater as the cost of peak power loads is disproportionately high.

4.2.2.2 Continuous mixer-extruder trials An important aspect of MRPRA's work has been the assessment of new continuous mixing-extruding machinery and processes to determine how well the new machinery is capable of safely mixing and extruding a range of typical NR compounds based on powdered rubber.

Four full scale trials have been carried out in conjunction with Farrel Bridge using their MVX machine and one trial has been carried out with Werner and Pfleiderer using their EVK machine. These have shown that the Farrel Bridge MVX (mixing, venting and extruding) machine is capable of continuously and safely mixing and extruding a range of Crusoe/N-765 SRF black mixes containing 25, 50 and 80 parts of black and convenient levels of oil (5, 10, 20 parts respectively) to give extrudates of good quality and appearance.

The Werner and Pfleiderer EVK 90 machine also gave extrudates of good quality and appearance with a similar set of Crusoe SRF black mixes, an oil extended SRF black mix and two oil extended calcium carbonate mixes.

The MVX machine has also given good extrudates with a highly loaded Crusoe-based flooring mix and an SBR flooring mix and safely and continuously mixed and extruded a natural rubber /56, N-330 HAF black/13, aromatic oil mix based on granulated SMR 10 rubber of 4, 8 and 10 mm particle diameter to give extrudates of good quality and appearance. This represents an advance in knowledge because NR particles of greater than 5 mm diameter had not previously been used. The MVX machine gave slightly less satisfactory results with brominated crumb rubber.

In most cases with the MVX machine, trials have been carried out with 400-500 kg of each powder blend and runs have exceeded one hour running times which would normally be long enough to reveal scorch and other problems.

Output and specific energies of mixing Summaries of the observed outputs and specific energies of mixing are outlined and compared with laboratory control mixes in Tables 5-8. Table 5 refers to MVX mixed Crusoe/N-765 SRF black mixes, Table 6 refers to EVK mixing with similar Crusoe/N-765 SRF black mixes and Crusoe calcium carbonate mixes, Table 7 refers to MVX mixing with Crusoe and SBR flooring mixes and Table 8 refers to MVX mixes based on N-330 HAF black and SMR 10 of varying particle size.

TABLE 5 OUTPUT RATES AND SPECIFIC ENERGIES OF MIXING FOR THE MVX MACHINE WITH CRUSOE SRF BLACK MIXES COMPARED WITH LABORATORY BR BANBURY MIXED POWDER BLEND CONTROLS

Crusoe powder	107	107	107
N-765 SRF black, pphr	25	50	80
Aromatic oil	5	10	20
MVX machine			
Output, kg/h	234-316	264-318	281-354
Output, Litre/h	212-287	225-273	230-289
Specific energy, kWh/kg	0.149-0.161	0.151-0.190	0.157-0.172
Specific energy, kWh/L	0.164-0.177	0.176-0.224	0.192-0.211
Laboratory BR Banbury (4 min mix cycle)			
Specific energy, kWh/kg	0.315-0.320	0.318	0.332-0.346
Specific energy, kWh/L	0.353-0.356	0.374	0.406-0.423

TABLE 6 OUTPUT RATES AND SPECIFIC ENERGIES OF MIXING FOR THE EVK MACHINE WITH CRUSOE SRF AND CALCIUM CARBONATE MIXES

Crusoe powder	107	107	107	107	100	100
N-765 SRF black	25	50	80	50	-	-
Aromatic oil	5	10	20	50	33	50
Calcium carbonate (Omyalite)	-	-	-	-	100	100
EVK 90 machine						
Output, kg/h	69-114	112-142	109-132	110	114-160	121-157
Output, litre/h	63-104	97-123	90-109	98	84-118	93-121
Specific energy, kWh/kg	0.40-0.58	0.35-0.44	0.39-0.41	0.27	0.23-0.28	0.24-0.32
Specific energy, kWh/L	0.44-0.64	0.41-0.51	0.48-0.50	0.31	0.31-0.38	0.32-0.42

TABLE 7 OUTPUT RATES AND SPECIFIC ENERGIES OF MIXING FOR THE MVX MACHINE WITH CRUSOE AND SBR FLOORING MIXES

Mix type	NR	SBR
MVX machine		
Rotor speed, rev/min	45-62	33-90
Output, kg/h	202-412	219-502
Output, Litre/h	118-253	135-304
Specific energy, kWh/kg	0.103-0.159	0.103-0.121
Specific energy, kWh/L	0.168-0.271	0.165-0.196

TABLE 8 OUTPUT RATES AND SPECIFIC ENERGIES OF MIXING FOR THE MVX MACHINE WITH HAF BLACK MIXES BASED ON SMR 10 OF VARYING PARTICLE SIZE COMPARED WITH LABORATORY BR BANBURY MIXED POWDERED RUBBER CONTROLS

4 mm particles	105	-	-
8 mm particles	-	105	-
10 mm particles	-	-	105
N-330 HAF black	56	56	56
Dutrex 729 oil	13	13	13
MVX machine			
Output, kg/h	131-335	185-342	158-379
Output, Litre/h	107-276	153-280	136-330
Specific energy, kWh/kg	0.155-0.243	0.159-0.240	0.159-0.277
Specific energy, kWh/L	0.188-0.298	0.193-0.293	0.183-0.264
Laboratory BR Banbury*			
Specific energy, kWh/kg	0.333	0.339	0.328
Specific energy, kWh/L	0.391	0.393	0.380

* 4 min mix cycle

Where comparative data is available in Tables 5 and 8 it is seen that the MVX mixer may use as little as a half the mixing energy required by a 4 min, single stage laboratory BR Banbury control mix. This implies a useful saving but it also implies that a shorter or less shear intensive, or less efficient mix process has been carried out.

Three of the Crusoe SRF black mixes are practically the same as those used for the MVX trial and they only differ in that a different Company's N-765 SRF black and a different grade of aromatic oil were used. It is thus possible to say from Tables 5 and 6 that the specific energy of mixing for the EVK machine is consistently higher than that of the MVX machine. The specific energies for the EVK mixes are also higher than the specific energies of the Banbury control mixes quoted in Table 5 which are relevant to both the EVK and MVX trials.

Uncured rubber properties In a set of MVX Crusoe/SRF black extrudates containing 25, 50 and 80 pphr black and in a set of MVX, granulated SMR 10/56 pphr HAF black extrudates using 4 mm, 8 mm and 10 mm granules it is clear that the MVX extrudates all had significantly higher Mooney viscosities and lower specific energies of mixing than relevant 4 min, single stage laboratory BR Banbury control mixes.

This observation indicates that the MVX gives a shorter or less intensive masticating action and mix process than the laboratory Banbury. It is consistent with lower mixing energy values already quoted.

In general the Mooney scorch times of MVX extrudates are similar to or a little lower than those of relevant Banbury control mixes. MVX and EVK extrudate temperatures are higher than conventional extrudate temperatures but lower than industrial internal mixer dump temperatures leading to the conclusion that it is wise to choose a safe curing system for continuous mixer-extrusion processes.

Vulcanized rubber properties All the MVX and EVK extrudates produced under a range of rotor or extruder screw speeds and output rates which have been compounded with a sulphur/CBS/Santogard PVI cure system proved safe enough for injection moulding with the REP B43K machine. All the extrudates derived from the Crusoe SRF black mixes gave a high level of vulcanizate properties which compared favourably with those of laboratory Banbury mixed controls made from the powder blends which went into the MVX. Although the extra processing by the REP machine may have masked some effects there were very few differences in vulcanizate properties between members of a series of injection mouldings which could be related to changes in MVX machine conditions of rotor speed and output.

A good example of observations over a wide range of rotor speeds is summarised in Table 9.

TABLE 9 EFFECT OF MVX ROTOR SPEED ON VULCANIZATE PROPERTIES[a]

MVX rotor speed rev/min	46	62	59	75	87	Banbury powder control[b]
TS, MPa	20.1	21.6	20.9	21.0	19.9	23.0
EB, %	425	473	455	460	441	496
M300, MPa	13.9	12.6	13.2	12.7	12.7	12.1
SG	1.227	1.209	1.213	1.211	1.214	1.172

[a] Mean of tensile properties measured along and at 90° to radial mould flow lines

[b] The powder control mix was sieved free of excess talc and therefore had a lower SG, lower modulus at 300% elongation and higher tensile strength and elongation at break

The output of the MVX machine therefore appears to be quite consistent in quality over a wide range of mixer section rotor speeds and output rates.

The MVX trial with various particle sizes of granulated SMR 10 was a joint trial with Dunlop Hose Division and Farrel Bridge. Dunlop Hose asked for an abrasion resistant mix which would have properties in between grades M24 and N17 BS490 conveyor belting specifications and which could be safely and continuously mixed and extruded on the MVX. Compounding studies using the laboratory BR Banbury and simulating the MVX process as closely as possible in rotor speed, chamber temperature and mixing times led to the following mix.

SMR 10 granules, 4, 8 or 10 mm	105
Dutrex 729 oil	13
Zinc oxide	5
Stearic acid	2
Flectol H	2
N-330 HAF black	56
CBS	0.6
Sulphur	2.6
PVI/50	0.8

Granulation and grinding of SMR 10 was carried out by Plascoat International Manhattan Mills, Stokesley, Yorkshire. Particle sizes chosen for examination were 4, 8 and 10 mm because NR particles of 5 mm diameter were known to process well on the MVX but there was no experience with NR of greater diameter.

Apart from extrudates based on the 10 mm particles, MVX extrudates gave lower tensile strength and elongation at break than control mixes. In most cases modulus at 300% elongation was higher. Observations of higher hardness, higher specific gravity, lower tensile strength, lower elongation at break and higher modulus are consistent with and are believed to be due to an excess of talc in the extrudates which had been sieved out of the laboratory control mixes.

As far as average values for tensile strength and elongation at break measured along and at 90° to radial injection mould flow lines are concerned, all MVX extrudates would pass BS 490:1972 Grade N17 belting specifications.

More than one ton of the extruded product from the joint trial was converted by Dunlop Hose Division into a high quality rock drill hose, the abrasion resistant pneumatic hose used in quarries. The process used was to put the extrudate on a warm-up mill and take it to their conventional extruder.

However, laboratory Banbury mixed control mixes prepared from 1.5 kg samples taken from the powder blends before they went to the MVX machine gave an exceedingly wide variation of unvulcanized and vulcanized rubber properties and are not quoted in detail here. Variations in specific gravity from 1.123-1.31 and variations in hardness from 51-92 indicated that one or more sources of variation could have contributed to the differences. Firstly, granulated rubber with an excess of talc could have separated out with the talc going to the bottom of the bag and led to an incorrect weighing of rubber and a variable ratio of rubber and talc in the final mix. An excess of talc is known to lead to high density and hardness and also a high concentration of curatives with respect to the rubber content. Secondly, separation after powder blending could have taken place during transit to the MVX and led to unrepresentative sampling and hence to variable mixes. Thirdly, simple weighing problems could have caused variations because it was clear that one batch of powder blend based on 10 mm particles contained practically no curatives. Fourthly, caking of carbon black and other heavy chemicals such as sulphur and zinc oxide on the walls of the powder blender by centrifugal force could upset the ratios of mix constituents.

In view of the wide variations in the mixes made from the powder blend samples it is remarkable that the MVX machine gave such a uniform set of extrudates. The variations in the data serve to emphasize the value of the Gardner blender which is part of the MVX machine and indicate the problems associated with transporting particulate material.

There were no serious problems of sampling, mixing and testing of black powder blends when the finer particles of Crusoe rubber (also transported a long way) were examined as controls for MVX extrusion experiments. It is interesting to speculate whether the larger particles of SMR 10 permitted a greater degree of separation during transport or whether the partition agent is more tightly held to the spray dried Crusoe particle.

Black dispersion of continuous mixer extrudates Throughout the work with powdered Crusoe rubber and granulated bale rubber a high level of vulcanizate properties has always been observed with due regard to the mix involved. It is therefore clear that if the technical properties of continuous mixer-extrusions pass relevant specifications for vulcanizate properties of products the new production method is satisfactory.

It should, however, be noted that carbon black dispersions have not been as good as one could have liked and this might limit the use of the mixer-extruder to products where good filler dispersion is not essential to high quality.

Cabot carbon black dispersion assessments on MVX extrudates made from SMR 10/HAF black mixes and injection mouldings made from them are difficult to make because the presence of talc spoils the assessment by causing holes in the microtome section. Mixes made from the smallest particles with more talc were more difficult to assess. Cabot ratings on extrudates were low, in the range E 1-4 to H 1-5, with the higher E ratings being observed in association with higher specific energies. These ratings were up-graded by the work done during injection moulding to ratings varying between C 1-4 and E 1-4 although some may not have been better than G or H 1-4. Cabot carbon black ratings of MVX extrudates with Crusoe mixes containing 50 pphr N-765 SRF black were in the range E 1-3 to H 1-4 but these were upgraded by injection moulding to D 1-3 to E 1-3. Single stage laboratory Banbury mixes of only 4 min duration gave slightly better Cabot ratings in the range C 1-3 to D 1-4 and these were upgraded to C 1-3 by injection moulding.

Cabot carbon black ratings on EVK extrudates with Crusoe mixes also containing 50 pphr N-765 SRF black were F 1-3 to G 1-3 and these were upgraded to B 1-C 1 by injection moulding. This data suggests that slightly better black dispersion is given by the EVK machine and this would be consistent with the higher specific energies.

More extensive discussions of mixer-extruder trials are to be found in the Second Progress Report (3.2) and the Third Progress Report (3.1) and appropriate Appendices.

4.2.3 Economics of production of powdered NR

4.2.3.1 Production in Malaysia The three types of free-flowing crumbs examined are as follows:-

1. Spray-dried Crumb Rubber, produced by spray-drying latex and using particulate partitioning agents to confer free-flowing characteristics.

2. Brominated Crumb Rubber, produced by surface-bromination of wet crumbs before drying.
3. Talced Crumb Rubber, produced by granulation of dry rubber extrudates and using talc as partitioning agent.

The flow-charts for the above types of free-flowing crumb rubber and bale SMR L are shown in Figure 7. The charts high-light only those salient features which have significant impact on the relative economics of the three processing routes.

The main features of the three types of free-flowing crumbs are summarised in Table 10.

TABLE 10 PARTITIONING AGENT, FREIGHT BULK DENSITY, PARTICLE SIZE AND STORAGE STABILITY OF FREE-FLOWING CRUMB RUBBER

	Spray-dried	Brominated	Talced
Partitioning agent	Silica, Silicates (7%)	Bromine (attached to rubber surface)	Talc (3%)
Freight bulk density*, kg/m^3	353.3	353.3	353.3
Particle size distribution	20% 2 to 4 mm 50% 1 to 2 mm 20% 0.5 to 1 mm 10% 0 to 0.5 mm	41% 4 to 6 mm 59% 2 to 4 mm	92% 2 to 5 mm 6% 1 to 2 mm 1% less than 1 mm
Storage stability (time to caking)	6 months	6-12 months (to be confirmed)	3 months

* The freight bulk density is obtained by dividing the weight of product by the volume of a standard pallet less the 16 cm allowance currently used in freight rate computations. For comparison, the freight bulk density of bale rubber (SMR) is 853.6 kg/m^3.

Capital cost Table 11 compares the capital cost of the free-flowing crumb processes with that of bale rubber (SMR L). The cost data are based on a factory with a monthly output of 250 tonnes. They apply to a situation where the factory is not too far from the latex source and the port. The cost of plant and machinery for the spray-drying process is about three times that of the other processes. This is mainly due to the extensive use of stainless steel equipment in the spray-drying plant. To compute the capital cost contribution to product cost, the spray-drying plant is amortised over 10 years while the other plants are amortised over 7 years. This approach goes part of the way to balance the disparity between the expected physical life of the machinery used. Amortising the spray-drying plant over 15 years will reduce its cost contribution from 15.6 to 12.6 cents per kg of crumb rubber produced.

TABLE 11 PLANT MACHINERY AND WORKING CAPITAL COSTS

	Crumb Rubber			
	Spray-dried	Brominated	Talced	Bale Rubber (SMR L)
Plant and Machinery				
- total (M$k)	2880.0	981.0	869.0	889.0
- contribution to product cost (M¢/kg)	15.6*	6.7	6.0	6.1
Working Capital				
- rubber (M$k)	747.6	755.3	732.5	755.3
- others (M$k)	544.7	405.3	356.6	163.0
- contribution to product cost (M¢/kg)	2.7	2.7	2.5	2.1

* Amortisation over 15 years rather than 10 years reduces contribution to 12.6 ¢/kg

<u>Product cost</u> The total product costs and cost components of free-flowing crumbs and bale SMR are given in Table 12.

The product cost of free-flowing crumb rubber substantially exceeds that of bale SMR L:

Spray-dried Crumb Rubber by M¢92/kg (27%)
Brominated Crumb Rubber by M¢66/kg (19%)
Talced Crumb Rubber by M¢43/kg (13%)

In the production of free-flowing crumbs, the chemical and packaging costs account for 55 to 74 per cent of direct costs. Partitioning agents account for 46 to 78 per cent of chemical costs.

Freighting rubber in crumb form costs M¢30 per kg more than that in bale form. The freight element accounts for 33 to 70 per cent of the difference in product cost between free-flowing crumb and bale SMR.

TABLE 12 PRODUCT (CIF) COSTS - M¢ PER KG

	Crumb Rubber			
	Spray-dried	Brominated	Talced	Bale Rubber (SMR L)
Product Cost (cif) made up of:-	429.59	403.48	380.98	337.68
a) rubber	278.07	286.00	277.42	286.00
b) direct cost	90.55	54.05	41.06	19.40
c) indirect cost	20.95	11.41	10.48	10.22
d) freight + insurance	52.02	52.02	52.02	22.06
e) less value of by-products	12.00			
Chemicals as % of (b)	55	27	13	14
Packaging as % of (b)	19	32	42	18
Partitioning agent as % of chemical cost	78	70	46	-

A RSS 1 price of M¢300 per kg is taken as base price.

Conclusion For general purpose applications, the crumb sizes of the three products are acceptable. The product cost differential between free-flowing crumb rubber and bale rubber (SMR) lies between 43 and 92 M¢ kg cif and has to be compared with the cost of mechanical granulation of bale rubber in the UK (see later) of ca £100/tonne (51 M¢/kg). As the cheapest form, talced crumb, is not suitable for freighting because of agglomeration it can be said that no powdered rubber produced in Malaysia can be exported economically. However, for use in the domestic manufacturing industry both talced crumb and brominated crumb are likely to be competitive with home produced mechanically granulated NR.

Fuller details of all the computations involved are to be found in the Third Progress Report (3.4, Appendices 1-9).

4.2.3.2 Production of mechanically granulated NR in the UK The cost of a new factory with new buildings and up-to-date machinery is considered in a 'green field' site near to London or the industrial centres of Manchester or Birmingham.

Processes A flow chart (Figure 8) indicates the steps required for a simple granulation process ending with a spectrum of medium sized particles such as obtained through a 7.93 mm (^{5}/16 in) screen. Particles of this size (about 62% in the range 4-8 mm diameter; 32% in the range 2.8-4 mm) are suitable for modern extruder mixers and conventional internal mixers. If smaller particles having a large proportion with a diameter of less than 2-3 mm are required for solution processes a more expensive and more sophisticated second granulator would be necessary.

If particles are required to pass stringent size specifications a mechanical sieve is required to separate over-sized and under-sized particles and return them to the granulator or reject them.

Capital cost Detailed capital costs for a building and machinery for granulating 250 tonne/month of NR are given in Table 13. The output of the hypothetical plant has been chosen to match the outputs of spray-dried powdered rubber, brominated granulated rubber, talced granulated rubber and SMR L control plants considered in the Third Progress Report (3.4).

It has a relatively high potential output compared with the current output of the three existing UK factories already carrying out this type of operation and it would be capable of granulating two thirds of the quantity of their combined total annual production but not the finer 1-2 or 3 mm granule production.

TABLE 13 CAPITAL COST OF GRANULATED RUBBER PLANT IN UK
APPROXIMATE OUTPUT : 250 TONNE/MONTH

	£
Main building, 250m^2 at £264/m^2	66 000
Bale cutter	8 000
Conveyor with weight sensor to feed bale slices to Blackfriars	3 500
Talc dispenser	9 000
Blackfriars 35 ASHD granulator	15 000
Pneumatic conveyor, cyclone	2 500
Filter bags	2 500
Centrifugal sifter	1 310
Bagging up equipment	4 500
Scales	800
Heat sealer for polythene bags	179
Shrink-wrap machine	365
Forklift truck	14 543
Office equipment	1 700
Installation (electrical and plumbing)	3 195
Total	133 092

<u>Product cost</u> Product costs are described as fully as possible in Table 14.

TABLE 14 PRODUCTION COSTS OF GRANULATED RUBBER IN THE UK

Direct costs/year	£	% of total	£/tonne of rubber in product
Rubber[a], 250 x 12 x £660	1 980 000	83.042	660.000
Partition agent[b], 250 x 12 x 0.05 x £88	13 200	0.221	4.40
Bags[c,1]	17 300	0.726	5.767
Polythene wrappers,[c,2]	6 000	0.252	2.000
Pallets[c,3]	30 000	1.258	10.000
Electricity[d]	15 376	0.645	5.125
Water[e]	1 500	0.063	0.500
Transport in + port charges[f], 188 x £175	32 900	1.380	10.967
Transport out[g]	75 000	3.146	25.000
Labour[h]	37 195	1.560	12.398
Testing charges[i]	772	0.032	0.257
Total direct costs/year	2 209 243	92.325	736.414
Indirect, overhead costs/year			
Factory administration[j]	37 195	1.560	12.398
Building, machinery maintenance[k]	6 495	0.272	2.165
Building capital charge[l]	13 554	0.568	4.518
Machinery capital charge[m]	22 434	0.941	7.478
Working capital costs[n]	101 929	4.275	33.976
Factory heating[o]	1 346	0.056	0.449
Factory lighting[p]	63	0.003	0.021
Total indirect costs/year	183 016	7.675	61.005
Total direct and indirect costs/year	2 392 259	100.000	797.419

Note and assumptions are to be found in the Fourth Progress Report (3.1 Appendices)

From Table 14 the total direct and indirect costs of granulated rubber are £797/tonne. Taking away the cost of the rubber (£660/tonne), the transport-in and port charge (£11/tonne) and the transport-out or delivery charge (£25.00/tonne), the cost of the granulation process is £101/tonne or approximately £100/tonne.

The cost of the granulation process quoted above contains no profit element for the granulator. If 'in house' granulation were carried out by a user in an established factory then further costs can be deleted from Table 14, eg pallets, wrappers, factory administration and a good portion of working capital costs so that an overall cost of granulation in such a situation would be nearer to £60/tonne. These figures are reasonably consistent with prices charged for granulation by three UK granulating companies all of whom are believed to be using machinery which is about 6-8 years old. L. Stechler and Co. charge £84/tonne for similar sized particles in bags and £132/tonne if the granules are packed in cardboard cartons. Transport is believed to be supplied by the customer. Telford Rubber Processors quote £67/tonne with extra for packaging and transport. Plascoat International, Manhattan Mills quote £110/tonne for granules including up to 10% talc.

The costs of the forms of powdered rubber exported from Malaysia and delivered to a customer in the UK can now be directly compared with that of mechanically granulated rubber made in the UK. (Table 15).

TABLE 15 COMPARISON OF COSTS OF POWDERED NR

	Powdered NR				Bale NR
	Spray dried	Brominated crumb	Talced crumb	Granulated	SMR L
£/tonne delivered	864	813	768	797	671

4.2.4 Economics of processing of powdered NR

Thus study compares the costs of production of rubber strip by the classical Banbury mix process using bale rubber and the new continuous MVX mixer-extruder process starting with granulated rubber. The strip considered is to be suitable for (1) feeding to extruders for further processing into products such as hose, cable covers, tyre beading or profiles or (2) feeding to injection moulding machines or (3) for use as moulding blanks for compression moulding. The MVX machine is capable of direct production of profiles or hose products and this also is considered in the costing study.

A hypothetical factory is considered which will use 250 tonne/month of bale or powdered rubber in line with the output of the rubber granulating process considered earlier.

4.2.4.1 Internal mixer process Rubber enters the factory in bale form. It is warmed for 3-5 days in a hot room and then weighed and mixed in a Banbury mixer with black fillers and other chemicals. The mix is dumped on to a 1 500 mm (60 in) mill and sheeted off. At this stage the sheet could be taken off in a wide sheet or this wide sheet could be cut into the final narrow webbed strips 100-150 mm (4-6 in) wide to feed to the extruder in the subsequent process. The wide strip or the loosely connected multiple narrow strips are cooled and stacked on pallets in 0.5-1 tonne loads. Narrow strips of required thickness and width can be produced by this method if the single pass (one-stage) mix process gives a product which is satisfactory in viscosity, black dispersion and the physical properties of a vulcanized product made from it.

The single pass method of mixing is not universal in use and, although it may be satisfactory in the case of some mixes, it may be necessary for the first stage product to be put back into the Banbury mixer for a further 2-3 min for (a) viscosity adjustment (b) improvement of black dispersion or (c) addition of curatives. In any of these three cases a wide strip would be cut from the mill under the Banbury and returned to the Banbury and the single production line would be adequate.

Alternatively adjustment of viscosity, improvement of black dispersion (or addition of curatives if necessary) could be carried out more economically on a 1 500 mm warm-up mill. Thus a second-stage production line is considered an essential part of the hypothetical factory design. In this case the wide strip is taken from storage pallets by a mill feeder and fed to the warm-up mill. The final narrow strips are cut off the mill, cooled in a narrow cooling bath and stacked by a wig-wag stacker for quality control and further processing.

4.2.4.2 Capital costs, internal mixer process Detailed capital costs for a building and machinery for producing about 20 tonne/day of rubber strips are given in Table 16 with notes and assumptions in the Fourth Progress Report (3.1. Appendix 2).

The emphasis in later discussion is on a Banbury mixer line supported by a second stage process line based on a warm-up mill. A less versatile but slightly cheaper alternative without the second stage process saves about 10% of the factory floor space and £100 000 of machinery.

4.2.4.3 Product costs, internal mixer process Product costs are described in Table 17 with notes and assumptions in the Fourth Progress Report (3.1. Appendix 3).

The main cost to consider is £748/tonne for rubber mix in strip form which results from a 3 min mix process followed by a second stage production line ('combined lines'). With NR at a cost of £660/tonne this process adds £88/tonne.

If it is possible that a 3 min mix process can be safely carried out on the F80 Banbury line without a second stage, the cost of the warm-up mill and subsequent production line can be neglected; labour, and about 10% of the factory space can be saved with a consequent reduction in product cost to £729/tonne. This rather risky, non-versatile production line could therefore save £19/tonne.

Alternatively, if a 3 min Banbury mix process is not long enough and the mix cycle has to be extended to 6 min, or, if the mix has to be put back into the Banbury for two, 3 min mix cycles another calculation can be carried out as in Table 17. The cost for a 6 min mix cycle (or two 3 min mix cycles) with use of the second stage production line is believed to form the upper limit of the possible range for the F80 Banbury process and this is £803/tonne. Doubling of the mix cycle time from 3 to 6 min therefore adds about £55/tonne to the cost of mixed rubber in strip form.

4.2.4.4 MVX, Mixing, venting, extruding process The process starts with rubber granules or powder which, for the sake of this exercise are assumed to be safely stored without agglomeration in bins from which they can be automatically fed and weighed into a hopper above a Fielder

TABLE 16 CAPITAL COST OF INTERNAL MIXER AND MILL FACILITIES TO PRODUCE A RUBBER STRIP FOR FURTHER PROCESSING

Usage of bale rubber : 10 tonne/day; 250 tonne/month

	£	£
Main building [a]		660 000
Main process line		
Bale cutter	8 000	
Automatic weighing and feeding	150 000	
Small powder weighments	7 000	
F80 Banbury	135 000	
1,60 in Mill under Banbury	56 000	
Batch-off machine) Festoon cooler) Wig-wag stacker)	40 000	
Strip cutting machine	10 000	
Pallets	2 500	
Fork lift truck	14 543	
Monsanto rheometer	11 020	
Mooney viscometer	8 865	
Office equipment	3 000	
Dust extraction	2 000	
Machinery, equipment total	447 928	
Installation, electrical, plumbing	22 396	
Main line total		470 324
Second stage process line		
Pallet unloader and mill feeder	10 000	
Warm-up mill, (60in)	56 000	
Strip cutter) Narrow cooler) Narrow conveyor) Narrow wig-wag stacker)	30 000	
Machinery total, 2nd stage	96 000	
Installation, electrical, plumbing	4 800	
Second stage line, total		100 800
Combined process lines, total		1 231 124

TABLE 17 PRODUCTION COSTS OF STRIP RUBBER MADE BY T
RAW RUBBER USAGE, 250 TONNE/MONTH.

Mix cycle assumption, min	3	3	
Direct costs/year	£	£	
	Main line	Second stage	
Rubber[a], 250 x 12 x £660	1 980 000		)
Dutrex 729 Oil[b]	81 900		)
Zinc oxide[b]	72 000		)
Stearic acid[b]	24 840		)
Antiozonant, IPPD[b]	198 600		)
N-330 HAF black[b]	583 080		)
Accelerator, CBS[b]	44 430		)
Sulphur[b]	126 360		)
Santogard PVI[b]	82 440		)
Electricity[c]	40 000	11 400	
Water[d]	18 346	8 315	
Transport in and port charges[e]	32 900		
Labour[f]	71 330	28 532	
Testing[g] (labour, 2 men)	28 532		
Total direct costs/year	3 384 758		
Indirect, overhead costs/year			
Factory administration[h]	99 862		
Building capital charge[i]	121 982	13 553	
Machinery capital charge[j]	157 268	33 706	
Working capital costs[k]	159 683		
Factory heating[l]	12 105	1 345	
Factory lighting[m]	563	62	
Machinery, building maintenance[n]	52 096	8 100	
Total indirect costs/year	603 559		
Total direct and indirect costs/year	3 988 317		

HE BANBURY PROCESS FOR FURTHER PROCESSING.

3 £ Combined lines	6 £ Combined lines	3 £/Tonne Main line	3 £/Tonne Combined lines	6 £/Tonne Combined lines
		361.97	361.97	361.97
		14.97	14.97	14.97
		13.16	13.16	13.16
		4.54	4.54	4.54
		36.31	36.31	36.31
→	→	106.60	106.60	106.60
		8.12	8.12	8.12
		23.10	23.10	23.10
		15.07	15.07	15.07
51 400	103 000	7.31	9.40	18.83
26 661	53 323	3.35	4.87	9.75
→	→	6.01	6.01	6.01
99 862	214 040	13.04	18.26	39.13
→	61 154	5.22	5.22	11.18
3 433 005	3 658 067	618.79	627.61	668.75
→	→	18.26	18.26	18.26
135 535	135 535	22.30	24.78	24.78
190 974	190 974	28.75	34.91	34.91
→	→	29.19	29.19	29.19
13 450	26 900	2.21	2.46	4.92
625	1 250	0.10	0.11	0.23
60 196	120 392	9.52	11.00	22.01
660 325	734 596	110.34	120.72	134.30
4 093 330	4 392 663	729.13	748.32	803.05

powder blender. Other powders and fillers such as carbon black are also assumed to be automatically weighed into the same hopper. Small quantity powders such as sulphur, accelerators, retarders and antioxidants still need to be manually weighed into the same hopper. The hopper can be filled while the previous batch is blended.

The hopper discharges into the powder blender and is loosely mixed by high speed rotation of paddles in the bowl of the blender. The free flowing, dry powder blend is then discharged into a storage bunker ready for feeding to the MVX continuous mixer-extruder.

The MVX machine compacts the free flowing powder, vents it under vacuum to remove air and moisture, mixes it to a homogeneous rubber mix and extrudes it in a section suitable for a finished profile or a strip suitable for a further extrusion, injection or moulding process.

4.2.6.5 Capital costs, MVX process To be consistent with the Banbury production exercise the same volume production target is considered.

There are two MVX machines available and these lead to a number of different strategies for achieving the production target depending on output and hours worked.

The small MVX 134/120 machine is known to MRPRA as a result of several sets of experiments. The output range with the mix under consideration when prepared with three different particle sizes (4, 8 and 10 mm) of granulated rubber was 107-330 litre/h. The optimum output for two particle sizes was about 278 litre/h and that for the third particle size was 330 litre/h. The range of output for Crusoe powder mixes with different black levels was 212-289 litre/h. The range of output for an NR flooring mix was 118-253 litre/h. Therefore the most likely output range of the MVX 134/120 machine is 250-300 litre/h.

To examine the potential annual output of the MVX 134/120 machine, production rates of 250, 300, 350 and 400 litre/h have been considered in preliminary calculations. The larger 240/150 MVX machine is less well known and annual output calculations have therefore been carried out using Farrel Bridge literature output figures in the range of 500-1000 l/h.

Conclusions were that further cost calculations should be based on hypothetical factories containing either 3 or 2 MVX 134/120 machines and 2 or 1, MVX 240/150 machines.

Details of capital costs for possible MVX factories are given in Table 18 and further details are discussed in the Fourth Progress Report (3.1. Appendix 4).

It is seen that the possible MVX machine factories are more expensive than the Banbury factory if two or three MVX machines are required to give comparable output. If only one MVX machine will match the Banbury output some capital saving can be made. Unfortunately the possible savings in machine space are likely to be exceeded by an increased requirement for storage space for raw rubber granules which take twice as much space as bale rubber.

TABLE 18 CAPITAL COST OF MIXING FACILITIES TO PRODUCE RUBBER STRIP BY MVX MACHINES

Usage of granulated rubber: 250 tonne/month

Machine options				
MVX 134/120	3	2	-	-
MVX 240/150	-	-	2	1
Main building[a]	719 136	668 448	668 448	617 760
Automatic weighing, feeding	150 000	→	→	→
Powder blender	15 278	→	→	→
Dust hood	2 000	→	→	→
Storage bunker and conveyor	39 000	26 000	30 000	15 000
MVX 134/120	384 000	256 000	-	-
MVX 240/150	-	-	296 000	148 000
Cooling conveyor	63 000	42 000	42 000	21 000
Pull rolls, output conveyor and wig-wag	18 000	12 000	12 000	6 000
Pallets	2 500	→	→	→
Fork lift truck	14 543	→	→	→
Monsanto Rheometer	11 020	→	→	→
Mooney viscometer	8 865	→	→	→
Office equipment	3 000	→	→	→
Installation	35 560	27 160	29 360	19 860
Total	1 465 902	1 238 814	1 285 014	1 034 826

4.2.4.6 Product costs, MVX process Product costs vary with the number of MVX machines, their output and the number of shifts worked. They also depend on man-power per MVX machine. Details of costing involving these variables are given in Table 19.

The MVX 134/120 machine is known by experimental work to give an output of about 250-300 litre/h (290-348 kg/h) with the NR mix (density 1.16 Mg/m^3) under consideration. At an output of 300 litre/h three MVX machines working 3 shifts/day are necessary to match the Banbury output and the associated cost of rubber strip is £832/tonne with 2 men to weigh and work the powder blender and 3 men per MVX machine. If the man-power can be reduced to one man for weighing and operating the powder blender and one man per MVX machine as suggested by Farrel Bridge the cost can be reduced to £807/tonne.

During trials it was desirable, if not absolutely necessary to have a three man team on the MVX machine. One man feeds the MVX, one operates it and one takes away the product. It is not unreasonable to suppose a good element of automation in weighing with the machinery costed here but one man must still weigh sulphur and accelerators. The same man could operate the powder blender and one can assume automatic feeding for the MVX.

Other costs for MVX 134/120 machine variations are more speculative on account of the high output rates but, if an output of 400 l/h is possible, the production costs could be reduced to £806/tonne for a 3 man MVX team or £787/tonne with a single MVX operator.

Costs for the bigger MVX 240/150 machine are speculative because this machine has not been tried yet. However, costs of strip could be from £804/tonne down to £763/tonne depending on output rates and manning levels.

4.2.4.7 Comparison of product costs, Banbury vs MVX Selected Banbury product costs are reproduced in Table 20 and compared with a range of possible MVX costs.

This table shows that at the most likely three MVX 134/120 machine output rate for the natural rubber mix under consideration the product cost exceeds the upper limit for the Banbury product cost. Even with only

TABLE 19 PRODUCTION COSTS OF STRIP RUBBER MADE BY THE MVX METHOD.

Equivalent raw rubber granule usage, 250 tonne/month

Machine options, MVX	← 134/120			→	← 240/150		→
Output per machine,* litre/h	250	300	350	400	500	750	1 000
Machines	3	3	2	2	2	1	1
Shifts/day	3	3	3	3	2	3	2
Overtime, h	758	-	1 215	358	1 039	758	1 039
Direct costs/year, £							
Rubber granules[a], (5% talc) (250 x 1.05 x 12 x £735.64!)	2 317 259	⟶	⟶	⟶	⟶	⟶	⟶
Chemicals[b]	1 213 650	⟶	⟶	⟶	⟶	⟶	⟶
Electricity[c]	56 814	47 348	41 953	36 708	51 541	36 469	27 354
Water[d]	31 667	26 391	22 619	19 792	15 835	10 556	7 918
Labour[e] (2+3 men/MVX line)	252 117	220 849	197 068	171 358	138 248	114 599	86 405
Testing[f] (labour, 2 men)	45 839	40 154	49 267	42 839	34 563	45 839	34 563
Total direct costs/year	3 917 246	3 865 651	3 841 816	3 801 606	3 771 096	3 738 372	3 687 149
Cost, £/tonne	704	695	690	683	678	672	662
Indirect, overhead costs/year							
Factory administration[g]	99 862	⟶	⟶	⟶	⟶	⟶	⟶
Building capital charge[h]	147 679	147 679	137 270	137 270	137 270	126 861	126 861
Machinery capital charge[i]	249 705	249 705	190 720	190 720	206 168	139 459	139 459
Working capital costs[j]	181 923	⟶	⟶	⟶	⟶	⟶	⟶
Factory heating[k]	14 655	14 655	13 622	13 622	13 622	12 589	12 589
Factory lighting[l]	681	681	633	633	633	585	585
Machinery and building maintenance[m]	71 517	71 517	60 583	60 583	62 783	50 748	50 748
Total indirect costs/year	766 022	766 022	684 613	684 613	702 261	612 027	612 027
Total direct and indirect costs/year	4 683 368	4 631 673	4 526 429	4 486 219	4 473 357	4 350 399	4 299 126
Cost, £/tonne	841	832	813	806	804	782	772
Simplest assumption for labour saving:	Deduct labour above and substitute figures below						
Labour (1 man to weigh + 1/MVX line)	91 679	80 309	73 901	64 260	51 843	45 839	34 563
Total direct and indirect costs/year	4 522 930	4 491 133	4 403 262	4 379 121	4 386 952	4 281 639	4 247 334
Cost, £/tonne	813	807	791	787	788	769	763

* Assumed for calculation of working hours to meet production target

! In-house cost/tonne of granulated rubber containing 5% talc

See also Fourth Progress Report (3.1 Appendix 5) two MVX 134/120 machines at an optimistic output of 400 l/h the product cost is only just under the upper Banbury cost.

Similarly, two bigger MVX 240/150 machines working at a likely output of 500 l/h give a product cost which is just below the upper Banbury cost.

A single MVX 240/150 machine working at optimistically high output rates of 750 and 1000 l/h could give substantially lower product costs than the upper Banbury costs but even with the minimum of man-power the product cost is still above the most likely Banbury cost of £748/tonne.

TABLE 20 COMPARISON OF PRODUCT COSTS, BANBURY vs MVX

Cost	£/tonne	
Banbury mixing process		
3 min cycle with 2nd stage	748	(most likely cost)
3 min cycle without 2nd stage	729	(cheapest cost)
6 min cycle with 2nd stage	803	(upper cost limit)
MVX methods	3 men/MVX	1 man/MVX
3 MVX 134/120 machines		
Most likely output, 300 l/h	832	807
2 MVX 134/120 machines		
Possible output, 350 l/h	813	791
Optimistic output, 400 l/h	806	787
2 MVX 240/150 machines		
Output, 500 l/h	804	788
1 MVX 240/150 machine		
Output, 750 l/h	782	769
Most optimistic output, 1000 l/h	772	763

4.2.5 Comparison of the economics of vulcanization of a profile through a Banbury/cold feed extruder/LCM bath process and an MVX extruder-mixer/LCM process

The exercise of Section 4.2.4 is a little unfair to granulated rubber and the MVX machine in that it ignores the fact that the MVX could have produced an accurate profile or vulcanizable product instead of just a strip of uncritical dimensions.

In this present exercise it is assumed that the MVX machine produces a finished profile or product ready for passing to the LCM bath for vulcanization. Two cost features will be ignored in the interest of simplicity. One is the cost of expensive profile dies; the other is that the rate of production is not likely to be so high as in Section 4.2.4 if the product has to be dimensionally correct. The LCM vulcanization plant is assumed to be adjacent to the Banbury plant or the MVX plant and rubber is assumed to be passed direct from the MVX to the LCM bath.

4.2.5.1 Processes In the cold feed extruder/LCM process rubber strip via the bale source, the Banbury, the warm-up mill and strip cutting process is stored for quality control purposes. It is fed to a cold feed extruder and then, while still warm (90-100°C), it is fed directly into the liquid curing medium (LCM) salt bath at about 200°C in which vulcanization takes place. A cooling and washing bath at the end of the LCM bath cleans up the product and a haul-off machine removes it for pre-sale storage. Two 150 mm (6 in), cold feed extruders are considered necessary for an output of 5 470 tonne/year of an unspecified extruded product such as a profile. Two LCM baths are also necessary for this output. One man can run two extruders side by side and one man is necessary to look after the cured product from each LCM bath, eg a team of three men per shift.

In the MVX/LCM process the MVX machine is considered to produce directly a fully shaped profile fit for vulcanization. The extrudate while still warm (100-130°C) is passed directly to the LCM bath. This saves the labour and space involved in storage for quality control and may take the conventional quality control unnecessary unless samples can be taken at intervals without spoiling the product or the continuity of the process. At least two MVX machines and two LCM baths are necessary for the 5 566 tonne/year output.

One man is necessary to remove product from each LCM bath. For the present exercise a rather optimistic output of 350 l/h is assumed in order to keep the number of MVX and LCM machines down to two.

4.2.5.2 Capital costs Detailed capital costs for buildings and machinery are given in Table 21.

The building for the cold feed extruder/LCM process is bigger than that for the LCM bath by the amount necessary to house the two cold feed extruders. Costs are therefore higher and the machinery costs are also higher by the cost of the cold feed extruders.

TABLE 21 COMPARISON OF CAPITAL COSTS OF EXTRUSION AND VULCANIZATION FACILITIES FOR CONVERSION OF BANBURY PRODUCED STRIP INTO A CURED PROFILE AND VULCANIZATION OF A PROFILE STRAIGHT FROM THE MVX

Process	Banbury/cold feed extruder/LCM	MVX/LCM
	£	£
Main building	147 840	129 360
Two extruders	140 000	-
Two LCM baths	110 000	110 000
Pallets	10 000	10 000
Fork lift truck	14 543	14 543
Installation	13 227	6 227
Total	435 610	270 130

4.2.5.3 Product costs Detailed production costs are given in Table 22 with notes and assumptions in the Fourth Progress Report (3.1. Appendix 5).

Direct costs (electricity, water and labour) for the cold feed extruder/LCM process are higher than the LCM process costs and so are [illegible] of the indirect costs but in spite of this the overall cost of the bale rubber/Banbury/cold feed extruder/LCM product is £16/tonne cheaper than the granulated rubber/MVX/LCM product. Thus, although direct extrusion of a profile by the MVX machine and its subsequent vulcanization in an LCM bath is cheaper than cold feed extrusion and LCM curing of a similar product, the economies possible in this step do not quite offset the premium of about £100/tonne for granulated rubber. Assumption of higher outputs from the MVX lowers costs as in Tables 19 and 20 and would make the MVX process competitive.

	Bale rubber/ Banbury/ extruder/ LCM process	Granulated rubber MVX/LCM process
Total direct and indirect costs, £/tonne	861	877
Difference, £/tonne	16	

TABLE 22 COMPARISON OF PRODUCTION COSTS OF A VULCANIZED PRODUCT FROM A BANBURY/EXTRUDER/LCM PROCESS WITH THOSE OF AN MVX/LCM PROCESS

Process	Banbury/cold feed extruder/LCM	MVX/LCM
Direct costs/year	£	£
Rubber in strip form [a*]	4 093 310	4 403 263
Electricity [b]	86 949	48 945
Water [c]	26 329	18 095
Labour [d]	73 901	49 267
Total direct costs/year	4 280 489	4 519 570
" " "£/tonne	783	812
Indirect, overhead costs	£	£
Factory administration [e]	73 901	49 267
Building capital charge [f]	30 360	26 565
Machinery capital charge [g]	96 225	47 071
Working capital costs [h]	204 666	225 540
Factory heating [i]	3 013	2 636
Factory lighting [j]	140	123
Machinery, building maintenance [k]	21 119	13 195
Total indirect costs	429 424	364 397
" " " £/tonne	78.51	65.47
Total direct and indirect costs	4 709 913	4 883 967
Total cost, £/tonne	861	877

Difference = £16/tonne

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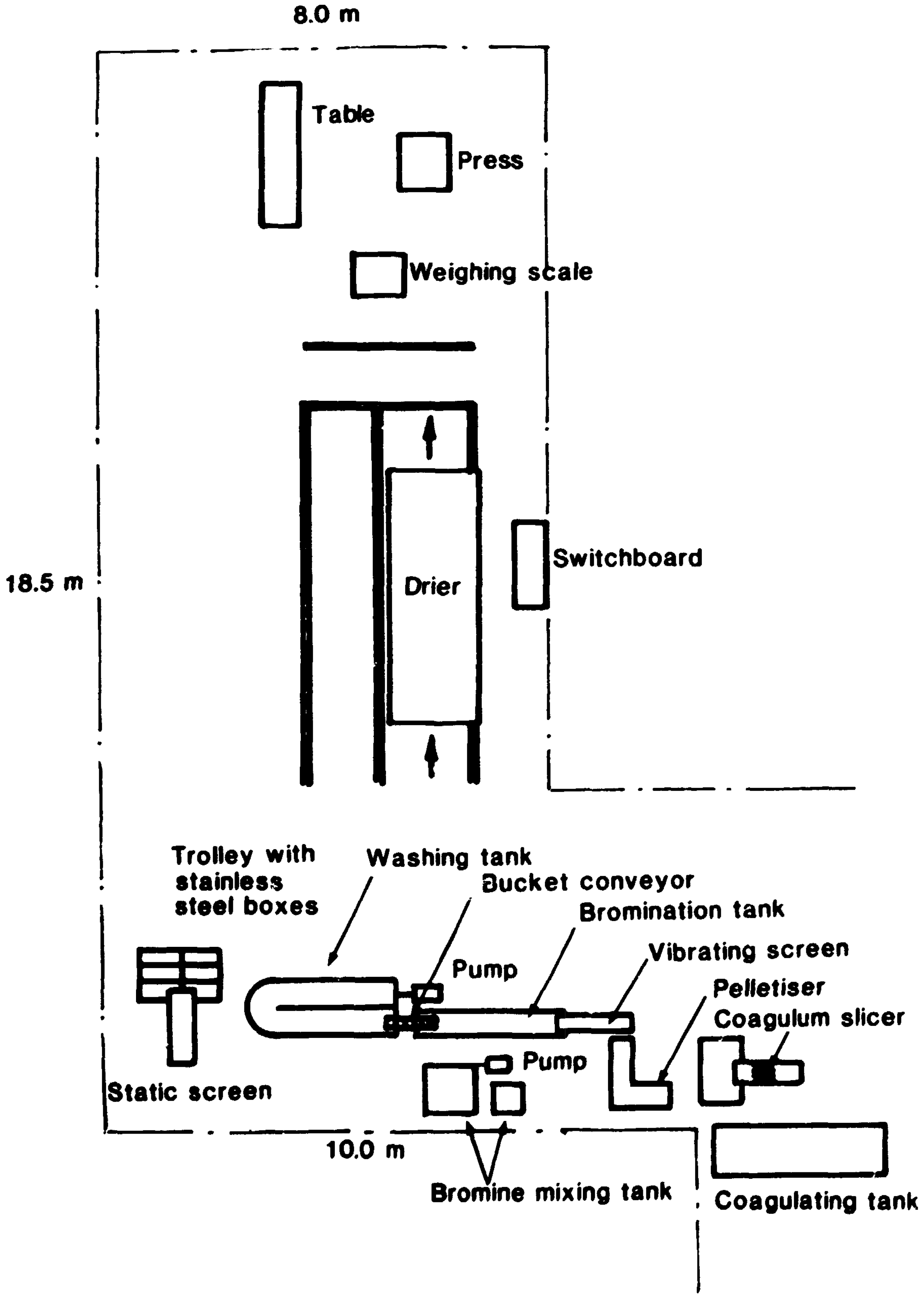
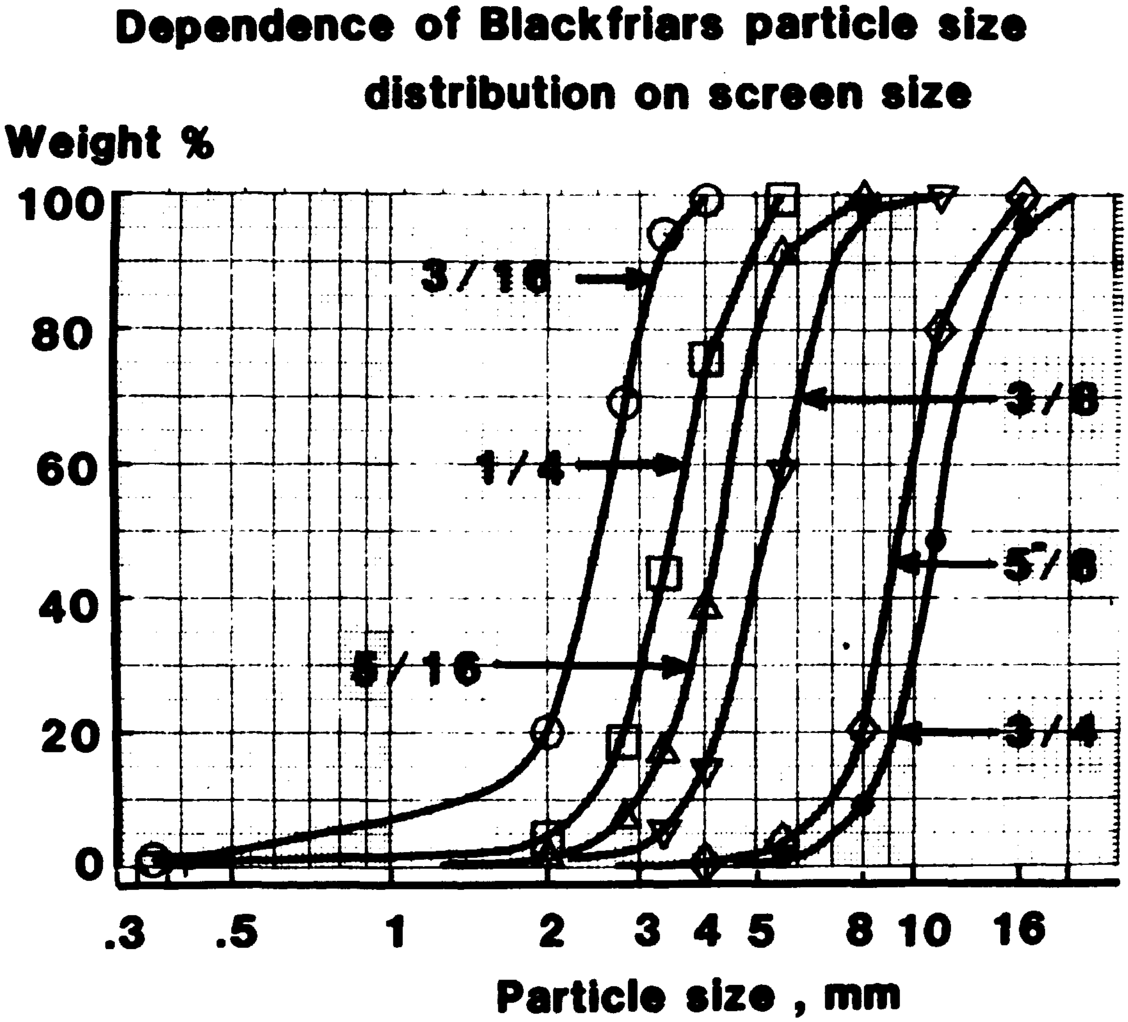
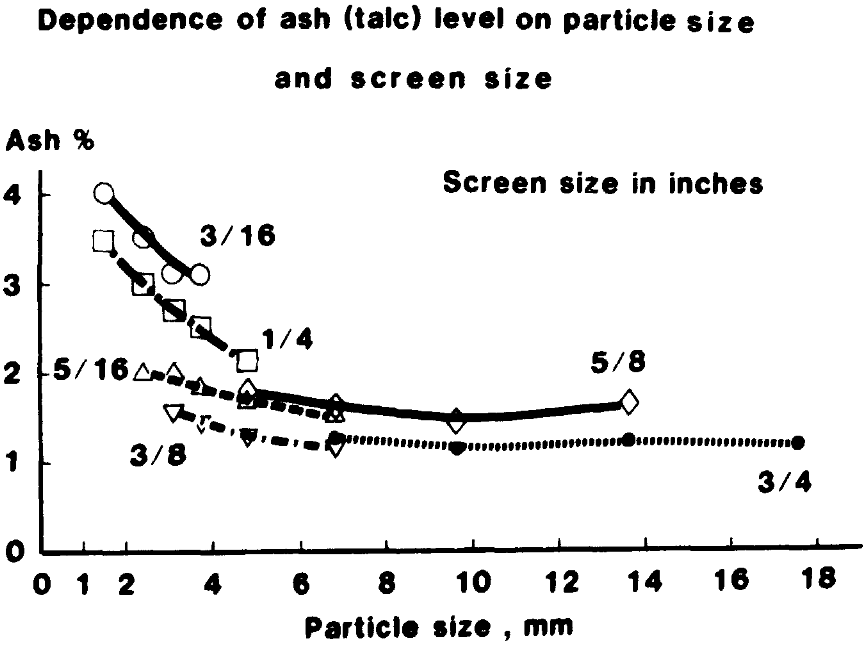
[*] Rubber in strip form from the Banbury and warm-up mill to the cold feed extruder and an extruded profile from the MVX to the LCM bath.

4. **Figure 1** Layout of brominated crumb rubber pilot plant.



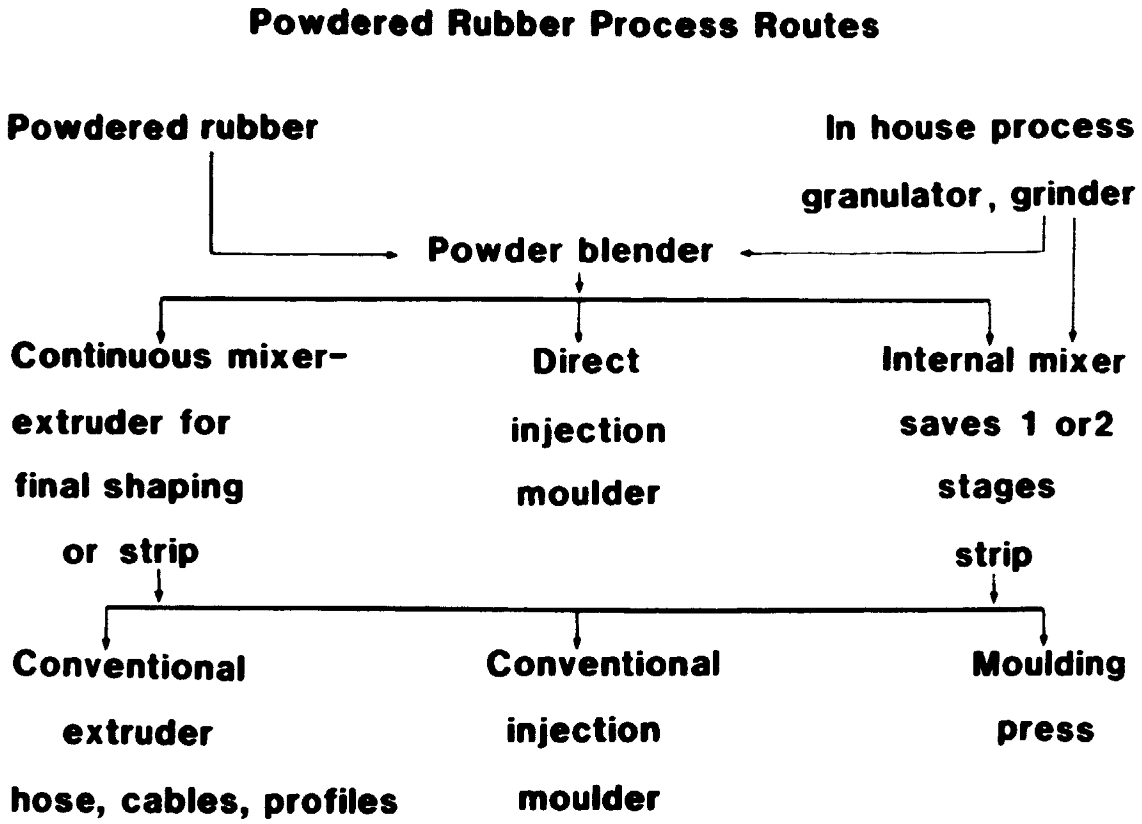
4. **Figure** 2 Particle size distribution versus screen size.

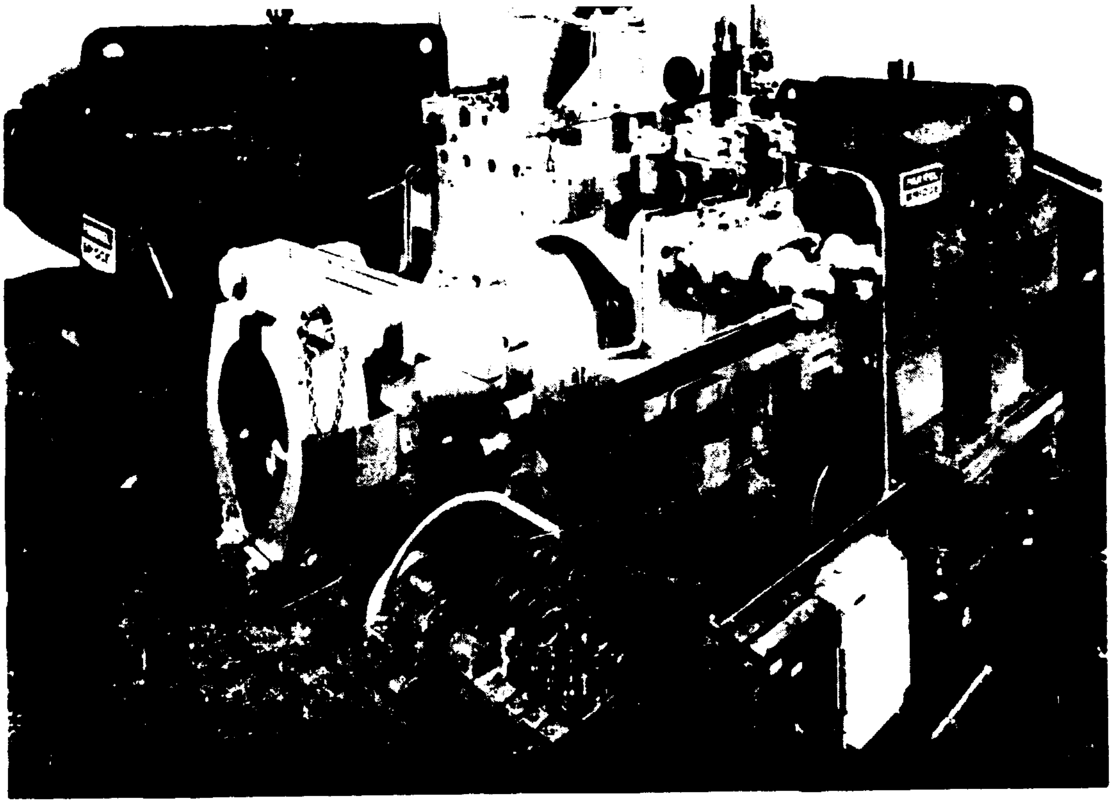




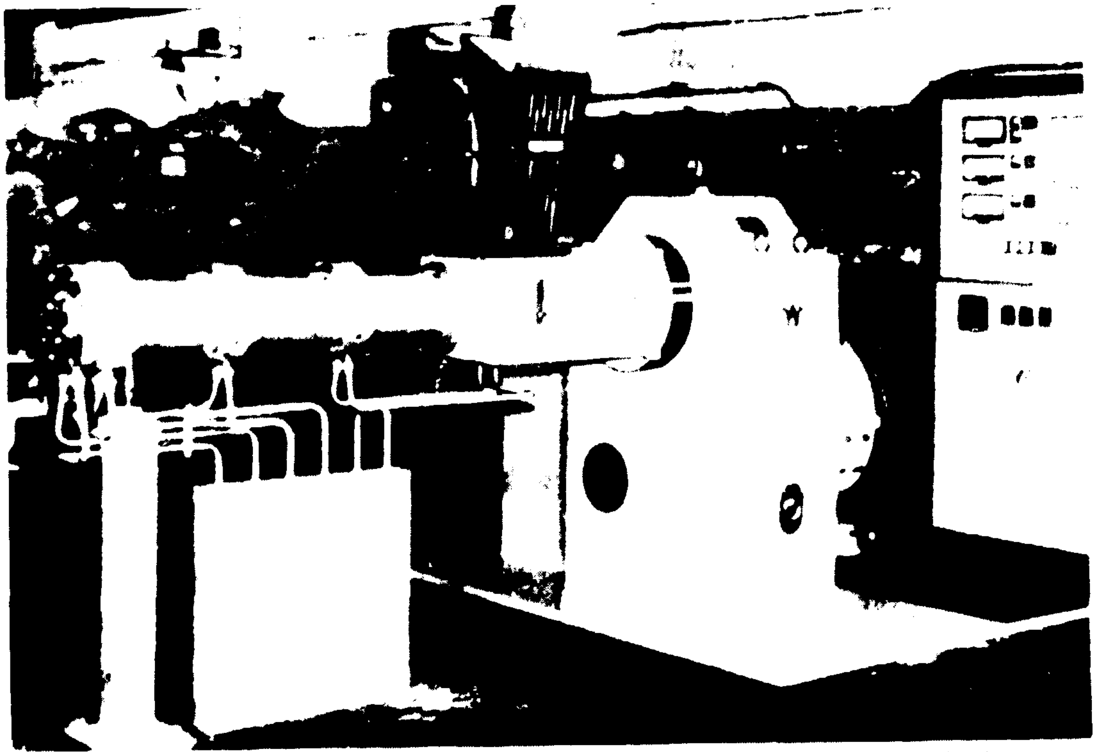
4. **Figure** 3 Talc (ash) levels versus screen size and particle size.

4. **Figure 4** Powdered rubber process routes.





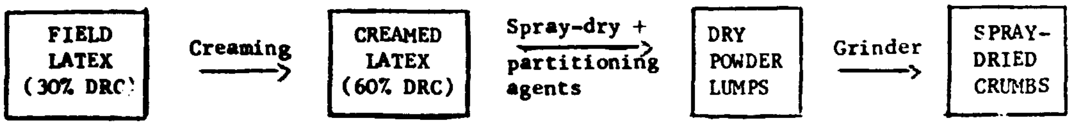
4. **Figure 5** The Farrel Bridge MVX machine (courtesy of Farrel Bridge).



4. **Figure 6** The Werner and Pfleiderer EVK machine (courtesy of Werner and Pfleiderer).

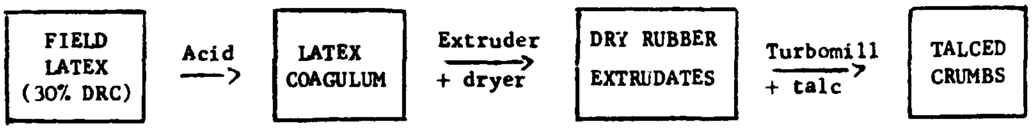
4. **Figure 7** Flow charts of free-flowing crumb and bale rubber processes.

(a) Spray-dried Crumb Rubber

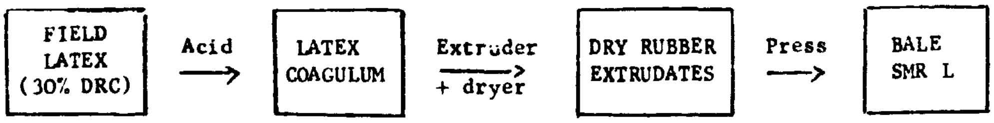


(b) Brominated Crumb Rubber

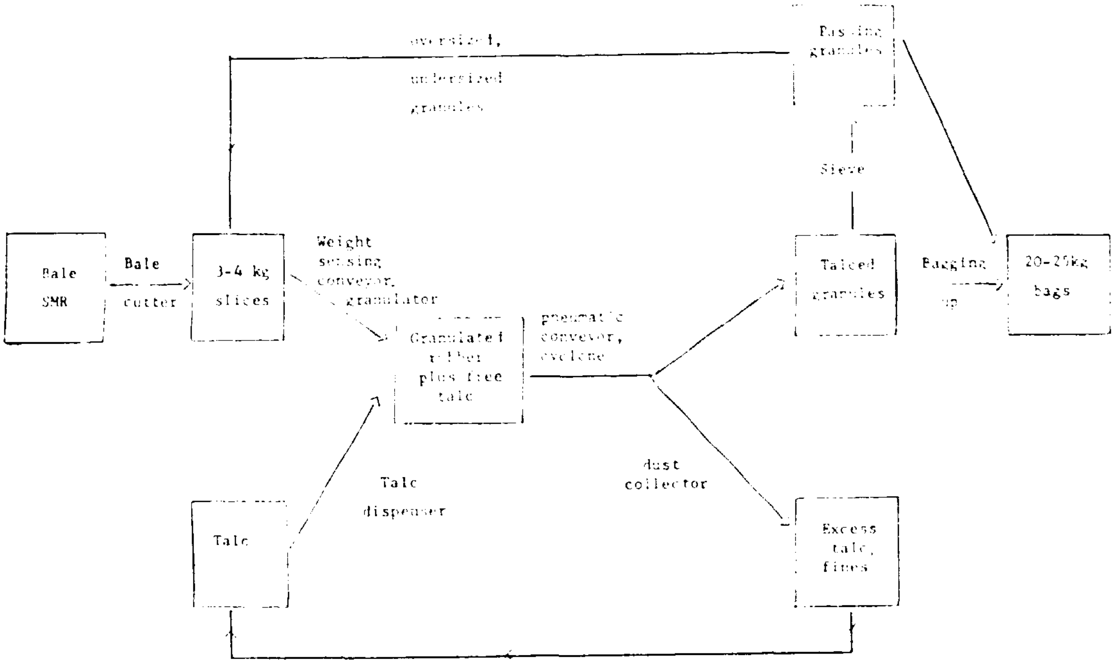
(c) Talced Crumb Rubber

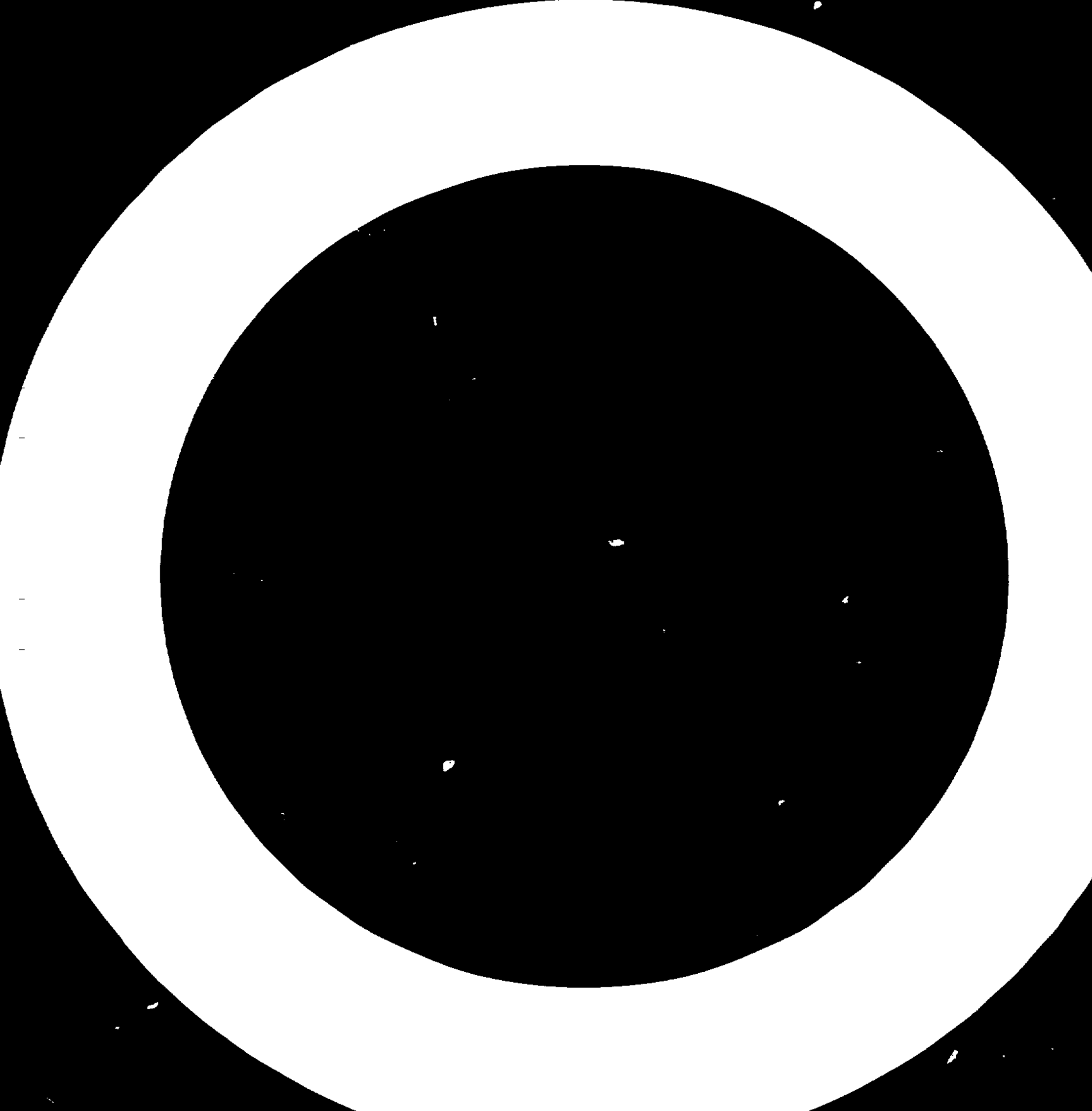


(d) Bale SMR L



4. **Figure 8** Flow chart for granulation of bale rubber.





5 CONCLUSION

5.1 THERMOPLASTIC NR GRAFTS

5.1.1 The concept that a comb graft of poly(styrene) on NR would behave as a thermoplastic rubber has been verified. The amount and molecular weight of the poly(styrene) which gives optimum physical properties has been determined. At this optimum the physical properties of the NR/poly(styrene) graft are similar to those of the established S-B-S thermoplastic block copolymers. The slight differences in behaviour reflect the different molecular structure and, probably, domain morphology of a graft versus a block copolymer.

5.1.2 To obtain such comb grafts, molecules of poly(styrene) of predetermined molecular weight have been equipped with a terminal functional group capable of adding easily and efficiently to NR. The azodicarboxylate group has been judged to be the best available choice in this respect.

5.1.3 The chemistry of the synthesis of azo-tipped poly(styrene) has been progressively simplified to give the cheapest route and at the same time scaled up to operate at the maximum batch size feasible in the laboratory pilot plant. Investigation of the economics of the process suggests that the cost of azopoly(styrene) will be low enough to make the NR/poly(styrene) grafts competitive in price with the synthetic block copolymers.

5.1.4 The grafting operation can be carried out by a simple dry-mixing of the two components with the same efficiency as grafting in solution and has been successfully and routinely operated in the Banbury internal mixer as well as in the small scale Torque Rheometer. The product can be compounded, also in the internal mixer, with oils, crystal poly(styrene), fillers etc to adjust its properties for specific applications and to cheapen it.

5.1.5 NR contains some non-rubber impurities which reduce grafting efficiency by reacting with or catalysing the decomposition of the azo function on the poly(styrene). This leads to an unpredictable variability in grafting efficiency between different grades of NR and between different batches of the same grade. The effect can be removed completely by extraction of the non-rubbers or in good part by the addition of Caloxol (calcium oxide). Some clues to the identity of the interfering material have been gained which may lead to a more radical solution to the problem.

5.1.6 Another problem which remains to be solved before a move to commercial operation can be recommended is that of an increased variability of the azo tipping of poly(styrene) as the scale of operation is increased. Although high efficiency is often achieved this cannot be guaranteed. There are indications as this is due to the inadequacy of laboratory handling methods on a large scale of production and that a move to methods of isolation and drying used industrially could overcome the problem.

5.1.7 The grafting principle has been successfully extended to poly(alphamethylstyrene) and poly(methylmethacrylate) and there is little doubt it could be applied to a wider range of polymers to give NR grafts with different and, perhaps, superior properties.

5.2 THERMOPLASTIC NR BLENDS

5.2.1 The high-shear blending of NR with poly(propylene) with or without the addition of minor amounts of a crosslinking agent gives a thermoplastic rubber. The material can be readily prepared on the tonnage scale using large internal mixers and has been successfully made by a custom mixer.

5.2.2 Tl TPNR blends range from hard rubbers to flexible plastics with flexural moduli readily controlled by the PP content. Their physical properties and ageing behaviour are as good as those of analogous synthetic materials usually based on EPDM and there is some advantage in better low-temperature impact resistance.

5.2.3 A detailed economic analysis has shown that TPNR blends will be cheaper than the EPDM-based materials in all areas other than the USA. This is especially so in the NR producing countries where production of TPNR blends for the manufacture of products for the domestic and export market should be initiated.

5.2.4 The TPNR blends are readily injection moulded and formulations and blending procedures have been optimised to give products of good surface finish and appearance. An odour typical of NR processed at high temperatures is the only disadvantage and this can be minimised in practice.

5.2.5 Extensive promotional work and large scale collaborative trials with potential users have been carried out. These have generally been successful and significant market interest has been generated for applications such as car bumpers and other automotive components, footwear, hoses, rail pads etc.

5.3 POWDERED NR

5.3.1 Powdered or granulated NR could be available in bulk quantities by several routes:- the spray drying of latex; the surface treatment (bromination) of crumb rubber; the mechanical granulation of bale rubber. Each form except the brominated crumb requires several per cent of a partitioning agent such as silica or talc to prevent agglomeration in storage or transport.

5.3.2 All these forms of powdered NR process readily in both conventional mixing equipment and the new mixer-extruders after powder blending. The size of the particles is unimportant up to 12 mm except for special processes such as dissolution in a solvent where fineness is an advantage. The mixer-extruders save on processing energy but filler dispersions in present machinery are adequate for general purpose applications and not for those demanding the highest strength and fatigue resistance.

5.3.3 An economic analysis has shown that freight costs make the export of powdered NR from NR producing countries uneconomic compared with the mechanical granulation of bale rubber in the consuming country. However the use of powdered NR (probably brominated or talced crumb) in modern powder-processing equipment could be advantageous in the rubber products manufacturing industry of the producing countries.

5.3.4 In consuming countries mechanically granulated NR will incur a premium of £100/tonne over bale rubber. If granulated 'in house' in the user's factory this premium could be reduced to £60.

5.3.5 Detailed product cost calculations based on a new factory equipped with either conventional mixing equipment or powder processing machinery of the same output indicate that although cost savings can be made with powdered NR these are generally not enough to offset the premium charged for this rubber. In special situations such as the direct extrusion of a finished profile a 'break even' point can be reached. It can be anticipated that as powder processing equipment is developed to become more cost effective then powdered NR will offer advantages over bale rubber, especially as the automation of factories will be facilitated by the use of continuous powder processes.