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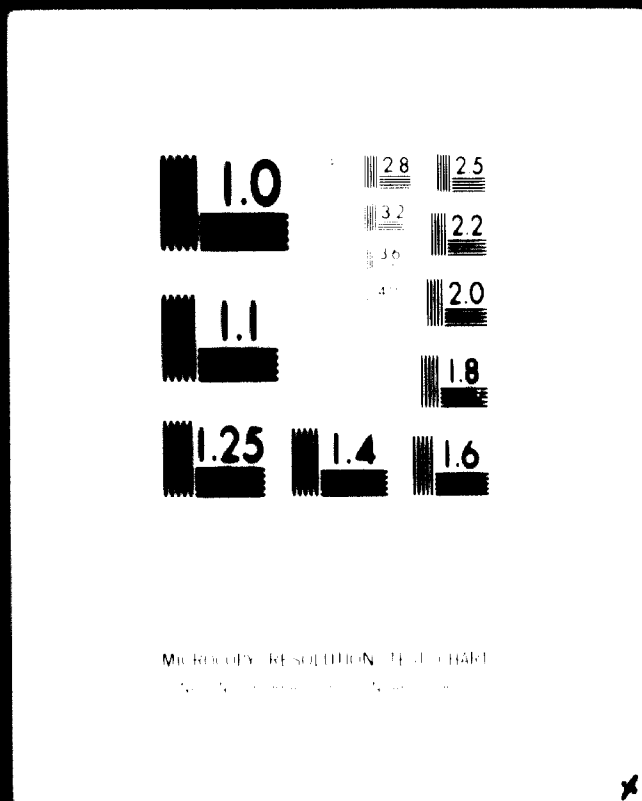
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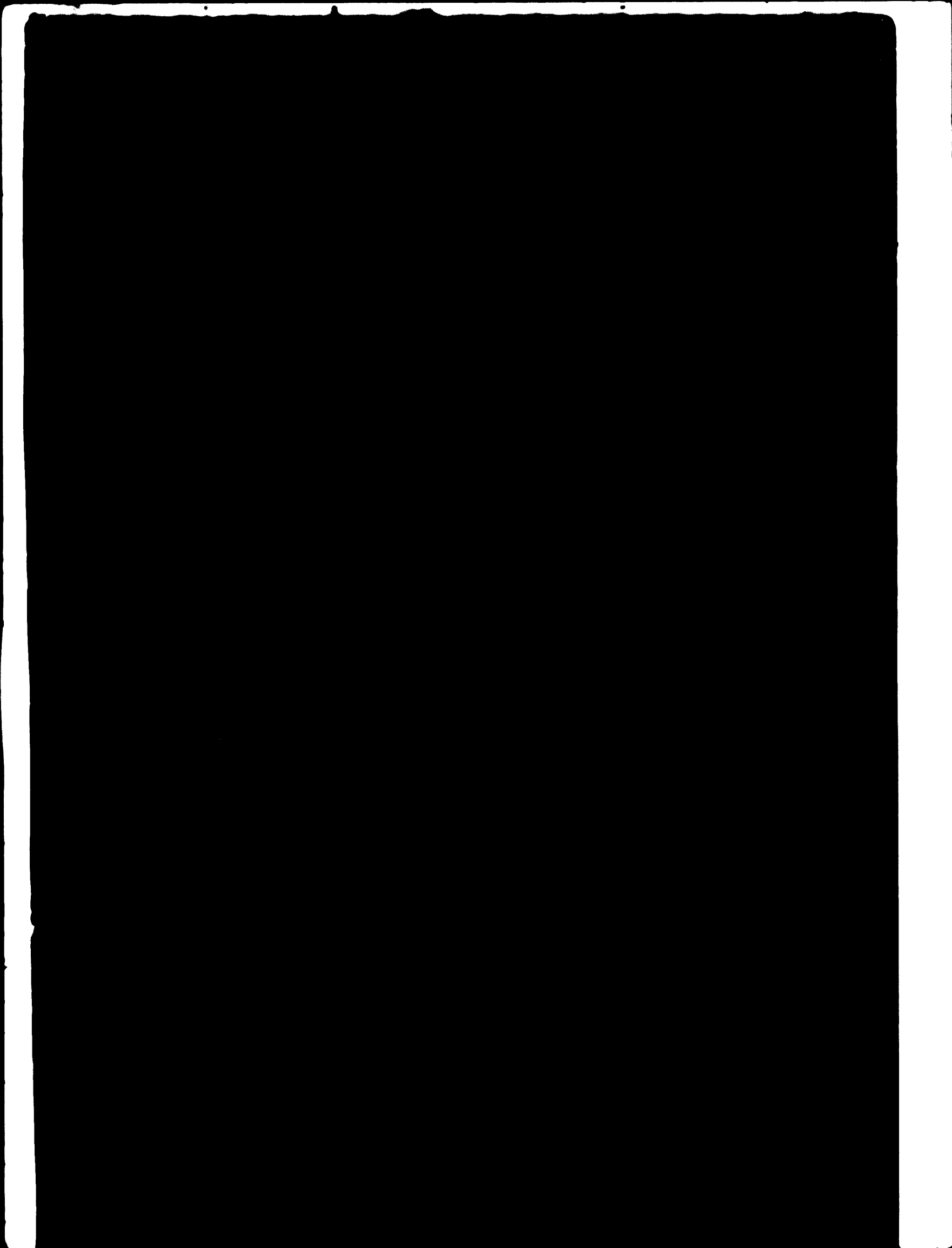
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DRAFT FINAL REPORT

of
PLASTICS TECHNOLOGY IN TRINIDAD AND TOBAGO ✓

by

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(TRI-081-SFB (SF/ID))

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D-1110

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SYNOPSIS

This report contains an account of the Project TRI-001-SFB (SF/ID) undertaken, over the period March to July, 1972, by United Nations Consultant in Plastics, J. E. S. Whitney.

The Plastics Industry of Trinidad and Tobago is surveyed, in relation to the delineation of possible areas for expansion and the role of the Caribbean Industrial Research Institute reviewed. Recommendations are made relevant to these aspects and further, short term United Nations assistance recommended.

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1.0

INTRODUCTION

The function of the expert, as set out in JOB DESCRIPTION TRI-081-SFB (SF/ID)

included:

Surveying the plastics processing industries of Trinidad & Tobago in order to assess their expansion potential and the potential for establishing new ones, with a view to:

1. Identifying various plastics products which should be considered for manufacture in Trinidad & Tobago and prepare an assessment of their economic feasibility.
2. Assess the potential market for such products not only in Trinidad & Tobago but also in the CARIFTA area and other countries.
3. Recommend an appropriate process, various raw-materials including those from the petrochemical industry, and equipment for the manufacture of such products.
4. Assess CARIRI's role in the promotion of the plastics industry and recommend various services which CARIRI should aim at offering, including the facilities needed for such services.

The following modifications were made to the Job Description which necessitated extending the duty tour from three months to four months.

1. In addition to visiting plastics processors visits were made to a representative selection of plastics consumers in order to facilitate the assessment of markets.
2. Concentrate upon and delineate those areas offering maximum potential for expansion, primarily in terms of import substitution.

3. The final results of the survey would be in the form of pre-feasibility recommendations rather than full scale feasibility studies.
4. Present a Seminar for CARIRI staff on the Classification and Major Applications of Plastics and reproduce it in a form suitable for internal publication.
5. Coordinate the organization of a one day Symposium on Plastics Technology containing contributions from the University of the West Indies and industry. Prepare a paper on "Reinforced Plastics" for contribution to the Symposium.
6. Subscribe to the public relations exercises designed to extend the knowledge of CARIRI's activities throughout industry by participating in radio and television broadcasts.

The expert would like to acknowledge the willing cooperation he received from all members of CARIRI staff and compliment the management on gathering together such an effective team. In particular his grateful thanks are due to the Director and Co-Director, Messrs. Eliv Sodahl and Hollis Charles; his counterparts, Messrs. Garry Voss and Sidney Thomas and the secretarial staff for their willing efforts in typing the Seminar papers, Symposium papers and this report.

2.0 SUMMARY OF RECOMMENDATIONS

.1 THERMOPLASTICS CONVERSION

- 2.1.1 As existing and intended converters already have plans for expansion and diversification expansion, at this stage, can reasonably be left to them.
- 2.1.2 A coordinating body should be formed for this sector to promote such activities as hire of injection and other moulds, dissemination of information as plant capacities and avoidance of over-duplication of products.

2.1.3 A feasibility study on the possibility of local manufacture of cast polymethyl methacrylate sheet in order to expand the already existing thermoforming applications by vertical integration.

2.2 SYNTHETIC RESIN MANUFACTURE

2.2.1 Feasibility studies on the possible establishment of a synthetic resin manufacturing unit (or units) for the manufacture of:

- a. Oil modified alkylid resins and unsaturated polyester resins.
- b. Vinyl polymer and co-polymer latices.

2.2.2 Prior to considering the feasibility of manufacturing phenolic and aminoplast resins either the manufacture of bagasse board and/or the manufacture of such thermosetting resin conversion products as decorative laminates and automotive filters, should become established.

2.2.3 Feasibility studies of the manufacture of decorative laminates and automotive filters, initially from imported pre-impregnated papers.

If these give a positive result the feasibility of establishing a paper and fabric impregnating unit should be studied.

2.3 THE ROLE OF CARIRI

2.3.1 CARIRI should maintain its effort to strengthen its liaison with educational and government bodies in order to maximise the use of its technical services. As an interim measure organize or collaborate in the organization of, symposia in plastics.

2.3.2 CARIRI should acquire and review their existing equipment against British Standard and A.S.T.M. specifications for plastics materials and products.

2.2.3 CARIRI should extend its patent information services by acquisition of selected British Patent Abridgement volumes, after having acquired and studied the Keyword and Classified Indices.

2.2.4 CARIRI should engage the services of a local industrial chemist, experienced in plastics technology.

2.4 FURTHER UNITED NATIONS ASSISTANCE

2.4.1 It is recommended that further short term assistance, in accordance with the Job Description set out on page 60 of this report be given to CARIRI.

MAIN SECTION

3.0 In conducting the survey of the Plastics Industry in Trinidad and Tobago a preliminary study of published statistics (1) revealed their inadequacy. Based upon the Standard Industrial Classification Code they are derived purely from data obtained from Customs & Excise, giving no direct indication of domestic production and grouping all imported plastics raw-materials together with certain plastics finished-products under one heading 'Synthetic Plastics Materials'. It was therefore deemed necessary to rely mainly upon information obtained during interviews in order to establish actual usage of plastics.

Published statistics have however been tabulated in Table 1 to indicate overall trends.

Per capita consumption of plastics, based upon aggregating items, 1 to 8, having deducted direct exports, has risen from 5.09 lbs. in 1966 (population assumed 994,850) to 19.4 lbs. in 1971 (population assumed 1,027,000). These figures are uncorrected as they include synthetic resins incorporated in paint and varnish media a high proportion of which is exported. Assuming an average synthetic resin content of 25% in

TABLE 1

IMPORT - EXPORT STATISTICS MATERIALS EMBODYING PLASTICS AND RESINS

A. IMPORTS (lbs x 1,000,000 unless otherwise stated)

<u>S.I.T.</u>	<u>Product</u>	<u>1966</u>	<u>1967</u>	<u>1968</u>	<u>1969</u>	<u>1970</u>	<u>1971</u>
599.01.01	Synthetic plastics materials.	3.651	5.038	5.029	9.451	10.614	10.602
599.01.02	Plastics sheeting for household use (Sq.yds x 1,000,000)	-	-	1.328	2.249	1.900	1.863
641.07	Impregnated and coated paper and paperboard (Includes laminates)	1.159	2.790	2.831	6.745	5.722	6.500
841.07	Plastic clothing	-	-	-	39.87	-	-
821.09.99	Plastic furniture	0.6676	0.7132	0.3925	0.173	0.105	0.122
661.09.091	Plastic building materials	-	-	0.0624	0.594	0.1909	0.1651
899.07.01	Plastic tableware	0.04086	0.06705	0.1184	0.1958	0.1379	0.1758
899.07.02	Plastic household articles	0.2430	0.2767	0.393	0.3754	0.6132	0.451

B. EXPORTS

599.01.01	Synthetic plastics materials	0.0656	0.0998	0.190	0.313	0.338	0.172
599.01.02	Plastic sheeting for domestic use (sq.yds x 1,000,000)	-	-	0.0018	0.0017	0.0007	0.0065
641.07	Impregnated and coated paper and paperboard	0.0049	0.0020	0.0026	0.0116	0.0397	0.0226
841.07	Plastic clothing	-	-	-	0.065	-	-
821.09.99	Plastic furniture	0.0167	0.1740	0.0870	0.0317	0.0206	0.0049
661.09.091	Plastic building materials	-	-	0.0002	0.0542	0.0357	0.0218
899.07.01	Plastic tableware	0.00784	0.00782	0.0207	0.0488	0.0406	0.0387
899.07.02	Plastic household articles	0.00351	0.00267	0.00139	0.00104	0.0165	0.0127

TOTALS (Excluding 599.01.02)

IMPORTS	5.161	8.253	8.472	17.535	17.583	18.014
EXPORTS	0.0985	0.1297	0.3019	0.4620	0.4911	0.2727
BALANCE (Imports over Exports)	5.063	8.123	8.170	17.073	17.092	17.741

exported paint and varnish media these figures are adjusted to 1.03 and 18.5 lbs. respectively. While even the revised figures cannot be regarded as having absolute meaning comparison of the 1966 figure with the per capita consumption in other developing countries (2) indicates that Trinidad and Tobago enjoys an averagely high consumption.

TABLE II. Plastics Consumption in 20 developing countries, 1966.

Country	Population (million)	Per Capita (lbs/head)	Country	Population (million)	Per Capita (lbs/head)
Algeria	12.1	1.57	Argentina	22.7	7.16
Brazil	83.1	1.90	China (Taiwan)	12.8	1.25
Columbia	20.3	1.98	Congo	16.0	0.52
Gambia	3.8	1.06	India	498	0.248
Indonesia	107.8	0.294	Iran	25.8	2.03
Kenya	9.6	6.85	Lebanon	2.5	12.4
Malaysia	96	0.679	Mexico	44.1	8.3
Morocco	13.7	1.72	Pakistan	105	0.366
Phillipines	33.4	3.3	Thailand	31.5	2.62
United Arab Republic	30.1	0.94	Venezuela	8.8	8.9

As a large proportion of the items imported under 599.01.01 are such that they may be converted and exported under other headings the figures for the balance of imports over exports do not give an accurate picture.

The apparent flattening of the growth curve from 1969 to 1971, in addition to reflecting the political disquiet occurring during this period, could also indicate possible approaching saturation of certain local markets. In particular, the sharp growth from 1966 could be indicative of the encroachment of plastics into fields previously held by traditional materials with a significant degree of saturation by 1969/71. This situation being typified by the use of decorative laminates in the manufacture of furniture. It can therefore be expected that future growth in such fields is likely to reflect a truer picture of actual market expansion.

The size of the Trinidad and Tobago market is such that, even allowing for the possibility of exporting to other CARIFTA and other countries within reasonable

distance; is such that for any particular item of manufacture only one manufacturing unit may enjoy viability. It is also necessary that the relatively high degree of protection such as is at present afforded, particularly during the initial stages of growth is maintained. Such protection, however, must be carefully gauged to ensure that it is not used to facilitate the manufacture of materials of inferior quality or at inflated prices.

The area surveyed can be conveniently sub-divided into thermoplastics conversion and fabrication products, classified in terms of processing techniques, and synthetic resin usage over a range of applications.

3.1 Thermoplastics Conversion Products

This section comprises the manufacture of products by moulding, extrusion and related processes in which the basic starting materials consist of imported compounded moulding powders. The forming, fabricating of imported sheet both imported and indigenously manufactured film, and the conversion of imported

fibres other than in the manufacture and conversion of synthetic fibre fabrics. For convenience the use of thermoplastics emulsions is discussed in Section 3.2 of this report.

Some twenty-one organizations involved in this sector were visited, ranging from relatively large concerns engaged in extrusion and moulding processes to small concerns engaged in relatively simple operations such as thermoforming.

In general the larger and medium organizations were found to be either affiliated to or subsidiaries of larger overseas concerns who in many cases exercised vigilance in respect of process control and quality control of finished products.

The same overseas organizations assumed a high degree of responsibility with regard to supervisory and operative training, particularly during the introductory stages of new product manufacture.

In the more capital intensive conversion processes, particularly injection moulding and extrusion, considerable concern was expressed regarding the high cost of such tools as moulds and dies in relation to the size of the local and CARIFTA markets.

Owing to the scarcity of trained toolmakers in Trinidad and Tobago almost complete reliance had to be placed on imported machinery and tools. Among the injection moulders some plans are already being made to exploit the possibility of obtaining moulds on a loan or exchange basis and undoubtedly such a practice should be pursued to maximum advantage.

3.1.1. Polyvinyl chloride and vinyl chloride co-polymers

3.1.1.1. Consumption and Trends

With current consumption of PVC compounds in plasticised and rigid PVC and vinylchloride-acetate co-polymer in the order of 1,250 tons p. a., all of which is imported, it is doubtful whether indigenous compounding would be justified at this time, particularly as it would involve heavy duty compounding equipment. No

examples were found of production involving the use of PVC pastes.

With the exception of gramophone record compounds, in which the scrap from de-
flashing and trimming was in the order of 35%, all respondents re-cycled a sub-
stantial proportion of their scrap.

A number of respondents had been in operation for a relatively short period, thus
the figures obtained are inadequate to provide meaningful forecasts of future PVC
consumption. Among the organizations which have commenced operation during
recent years, it has been the practice to initially cater for the Trinidad and Tobago
market then expand into the CARIFTA market. Expansion into other markets, such
as South America, is difficult as these are frequently highly protected by import
controls. This situation is paralleled with the other sections contained in this report.

Although with expansion in production of existing lines and diversification consumption

TABLE III

CONSUMPTION AND TRENDS IN POLYVINYL CHLORIDE AND VINYL CHLORIDE CO-POLYMERS

Visit Report No.	Raw Material and Form	Process	Finished Item	General Trends	Consumption (tons p.a.) 1971/72	Number of Plant Items	Working day	Capacity Utilization
3	Plasticised moulding powder	Extrusion	Garden hose	Fairly static expanding into profiles.	65	1	2 shifts	50%
9	Rigid PVC moulding powder	Extrusion	Pipe and Conduit	Commenced Dec. 1965 Doubled since 1967	500	1 (1965) 2 (1969)	3 shifts	70%
	-do-	Injection moulding	Pipe fittings	Commenced 1970		1 25 oz		
14	Plasticised moulding powder	Extrusion	Garden hose	Not important in light of other products	Est'd 80	1	3 shifts	100%
26	Plasticised PVC	Injection moulding	Shoes: Sports & Casuals	Supply only local market - have other CARIFTA factories	250 50	10	-	-
38	Plasticised moulding powder	Injection moulding	Sandals	Commenced 1967	60 Negligible resumed May 1972	2, multi stationed	1 shift	Potential cap. 250 t.p.a.
39	Plasticised moulding powder	Extrusion sheathing	Electric Wire and cable	Expansion in excess of 10% p.a.	250	1 x 90 mm 1 x 120 mm 1 small	3 shifts	Approaching 100% - expanding
41	Vinyl chloride-acetate co-polymer biscuits	Compression moulding	Gramophone records	Fairly Static	45	2 x LPS 2 x singles	1 shift	33%
Firms not visited:								
	Plasticised moulding	Injection moulding	Sports shoes	-	Est'd 200	-	-	-
	Gramophone records	Compression moulding	Gramophone records	-	Est'd 45	-	-	-
TOTAL COMPOUNDS					1,235			

of PVC compounds might well double during the next five years, it is not possible to foresee a likelihood of polymer manufacture being justified.

Imported PVC film and leathercloth is being used in a variety of fields, particularly in furniture manufacture (upholstery), household goods (tablecloths, curtaining etc.) and in automotive assembly (upholstery and linings). In the last instance it is imported in the form of shaped profiles sometimes high frequency bonded to a backing layer. This highfrequency welding technique has been established in Venezuela but it is understood that the plant is not working to capacity. A very minor interest has been expressed in manufacturing bags and inflatables by high frequency welding. In view of the scattered nature of the markets for film and leathercloth no specific study was made of this area. It was accepted that consumption was not adequate to justify indigenous manufacture in the light of the high capital intensity

3.1.0.2. Expansion plans

Certain organizations visited were either in the planning stage for increasing pro-

duction of items currently being manufactured or diversification into other lines.

The latter embodied the following proposals: Blow moulded bottles for soft drinks etc. A know-how deal is under consideration with an Austrian firm already manufacturing in Venezuela. This could also embrace such items as feeding bottles in polycarbonate. Another firm intends to install an additional machine specifically for this purpose.

Footwear: The firm manufacturing injection moulded PVC sandals is considering extending its equipment to handle expanded PVC and is acquiring a facility to manufacture PVC Wellington boots. In this latter item they consider that the market, mainly among oil-field workers and in agriculture could be in the order of 150,000 pairs.

Expansion in the capacity for insulated cable is also under consideration. Of perhaps the greatest importance has been the recent acquisition by one respondent of a Henschel High Speed Mixer. This is currently being used for their own powder blending of U-PVC

compounds on a limited scale but they foresee the possibility of extending its use to embrace compounding on a trade basis.

3.1.2. Polyolefines

Of the firms visited the total consumption of polyolefines is currently in the order of 2,135 tons p. a. distributed between :

Low Density Polythene	-	1,250 tons p. a.
High Density Polythene	-	725 " "
Polypropylene	-	160 " "

Despite the rapid growth in the manufacture of film it would appear that significant quantities continue to be imported in the form of film as such and in the form of simple bags. As by far the largest amount of this is for packaging purposes its use is distributed over a wide range of industries. In order that estimates could be made for the quantities involved it would be necessary to undertake a separate survey. On a quality basis it would appear that the clarity of indigenously produced LD polythene film is inferior to that of some imported grades. With the advent of new blown film extruders and the possibility of improving qualities the hitherto rapid

expansion in polythene film production should continue.

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During the survey one manufacturer interested in obtaining polypropylene battery boxes was visited. He was consequently put in touch with an injection moulder who had a machine of adequate shot weight capacity. The possibility of the battery manufacturer's parent company supplying the necessary moulds on a loan basis is now being considered.

High density polythene is finding extensive use in the manufacture of various bottles and containers. This market continues to expand not only from the aspect of import substitution but also with continuing encroachment into glass containers. One manufacturer is currently negotiating for the manufacture of magnesia and liver salts bottles in polythene.

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A major detergent manufacturer cannot completely obtain his requirements from local

sources and is continuing to import a proportion of his H. D. polythene bottle requirements.

Polypropylene and, to a lesser extent, high density polythene, are continuing to encroach upon the use of sisal and manilla in the manufacture of ropes and cordage. Currently however all the yarn used for this purpose is imported. The possibility of using indigenously manufactured twisted, fibrillated polypropylene film is being considered. The use of polypropylene monofilament yarn is confined to cordage applications where superior abrasion resistance is required.

The largest film manufacturer effected a considerable expansion in capacity by acquiring the lay-flat tubing plant of another manufacturer, when they went into liquidation. Thus, it is possible that their capital investment to production ratio contributed to their profitability.

In the production of polyolefine films, plants are distributed throughout the

TABLE IV

CONSUMPTION AND TRENDS IN POLYOLEFINES

Visit Report No.	Raw Material and Form	Process	Finished Item	General Trends	Consumption (tons p.a.) 1971/72	Number of Plant Items	Working days	Capacity Utilization
3	HD Polythene compound	Blow moulding	Bottles up to 1 quart	Production restricted by space considerations	75	2	2 shifts	-
13	HD Polythene } LD Polythene } compounds	-do-	Bottles 10 oz to 1 gal.	Commenced 1967/8. Forecast doubling by 1973/74.	150	-	-	-
14	LD Polythene compound	Lay-flat film extrusion	Film	Have expanded to full plant capacity.	1,000	4	3 shifts (7 day week)	100%
	HD Polythene compound	Injection moulding	Soft drink bottle cases and various household items.	Limitation by cost of moulds are investigating mould loaning.	500	1 x 350 m/c 1 x 900-4/lb shot (new)	-do-	-
	Polypropylene compound	Lay-flat	Tapes	Expanding well.	150	See above	-do-	See above
20	Polypropylene compound	Injection moulding	Coat hangers and tooth-brush handles etc.	With new machine consumption of pp should increase rapidly to 36 t.p.a.	10	1 x 1½ oz 1 x 5 oz (new) + 1 x lab. m/c	-	Fully occupied coming on stream
31	LD Polythene	Lay-flat	Film	Would not disclose.	240	1 x extruder sealer-cutter etc.	-	-
36	Polypropylene monofilament and fibrillated yarn. HD Polythene yarn	Twisting	Rope and Cordage	Progressive encroachment on natural fibres	90	Various of differing sizes	-	Substantially fully utilised
	HD Polythene	-do-	-do-	-do-	20			
44	LD Polythene film	Printing and welding	Packages and bags	Imported film growth from 60 t.p.a. 1969 to ----	240	Have on order two Lay-flat extruders	-	-

Caribbean and the North Eastern coast of South America. Thus markets tend to be somewhat geographically restricted. Currently there is no significant indigenous production of pigmented heavy gauge LD polythene film, most of it being imported from the Jamaican plant of a large manufacturing company, who although having a can manufacturing plant in Trinidad and wide interests in the plastics field in the United Kingdom, do not contemplate local plastics conversion.

3.1.1.2. Expansion plans and potentials

In the field of polyolefines it appears that the greatest interest in expansion by diversification lies in fibrillation of polypropylene and the manufacture of end products, such as, woven sacks therefrom. Such sacks have significant potential use in packaging commodities including sugar, fertilisers and bananas and are currently being imported under the trade name "Valeron".

One firm of sales and import agents intend to invest in plastics conversion and are currently negotiating with a Canadian organization which specialises in large

scale injection moulding, particularly household articles. The object of their association would be to obtain know-how and effect an interchange of moulds on a reciprocal contract hire basis. Planned production runs of 50,000 to 60,000 items per mould are envisaged with estimated sales rising to TT\$2,700,000 during the third year of operation. Although potentially using a variety of thermoplastics, the use of high density polythene, imported from Puerto Rico, would predominate.

3.1.3. Styrene polymers and copolymers

Although injection moulding of small items in general purpose grades of polystyrene is being carried out, it is on a comparatively small scale and caters for the local market almost exclusively. One item predominates, the disposable forks used for 'Chicken N Chips'. One small manufacturer, who is primarily a manufacturer of polymethylmethacrylate signs is successfully supplying the market in consequence of which he is likely to face competition in the near future as the market is probably insufficient for two moulders.

TABLE V

CONSUMPTION AND TRENDS IN STYRENE POLYMERS

Visit Report No.	Raw Material and Form	Process	Finished Item	General Trends	Consumption (tons p.a.) 1971/72	Number of Plant Items	Working day	Capacity Utilization
1	Formable beads	Expanded mouldings	Ice boxes, picnic ware, pipe lagging blocks (12' x 6' x 1')	Recent years: Exports constant, slight increase in local demand.	130	Expanders (5) Block moulds (4) Shaped articles: 1 press (semi auto) 1 press (fully auto)	1 shift	25%
14	Moulding powder (general purpose)	Injection moulding	Misc. small items for household ware	See 14. Table IV. Increasing capacity for small mouldings	90	See 14. Table IV + 1 n/c ordered		See 14. Table IV.
18	High Impact sheet	Vacuum forming	Refrigerator linings	From 12,000 units p.a. in 1971 to anticipated 40,000 + in 1974	300	1 rotary multi-station + 1 on order		
20	Moulding powder (general purpose)	Injection moulding	Disposable and various small items	Rapid growth in demand for "Chicken N Chips"	40	See 20. Table IV.		See 20. Table IV.
<u>Not Visited:</u>								
	High impact sheet	Vacuum forming	Air conditioning ancillaries		Est'd 50			
TOTAL -					610			
			Moulding powder		90			
			Sheet		390			
			Formable beads		130			

A plant for the manufacture of foamed polystyrene articles was established by a manufacturer who has since disposed of it to another organization and concentrated on the manufacture of foamed polyurethane. The second manufacturer appears to be successfully operating the process but is only utilising 25% of his potential capacity.

The demand for high-impact polystyrene sheet, particularly for vacuum formed refrigerator liners, has expanded rapidly and is confidently expected to continue to more than double by 1974.

Attempts have been made to produce injection moulded disposable cups, plates and snow cone cases from multi-impression moulds. These however did not show a high enough profitability and were abandoned about two years ago.

3.1.2.2. Expansion plans

Injection Moulding. One company is in the process of installing a 75 gm. moulding

machine to produce small items including combs, screwcap closures, industrial containers and pill boxes, mainly in general purpose and high impact polystyrene. They intend to order later this year a vacuum forming plant to produce containers for food etc. and bottles by the bonded halves technique.

A Pencil Factory, who have hitherto assembled ball point pens from imported components, are currently installing a machine to injection mould the clear barrels.

Two Sign Manufacturers have ordered injection moulding equipment (6 oz. shot weight) to produce disposable forks, ice cream cups etc.

Sheet Extrusion and Vacuum Forming

Two organizations are considering the manufacture of expanded polystyrene sheet, by the annular extrusion process, for vacuum forming. One company intends to start vacuum forming egg boxes, and drinking cups first from imported sheet before finalising on manufacturing their own sheet.

One firm is considering extruding High impact polystyrene sheet initially for its own conversion and then for the local market. In this project it is possible, however, that they may seek the collaboration of a prominent extruding organization.

Both sign manufacturers who are currently vacuum forming PMMA are considering extending their operations to include vacuum forming articles from ABS and High impact polystyrene.

One firm who is at present solely concerned with paper conversion (cartons, drinking straws etc.) is currently negotiating for the purchase of equipment to manufacture drinking straws in High impact polystyrene. They are also purchasing vacuum forming equipment for drinking cups which will most probably be fabricated from polythene and polypropylene.

3.1.4. Polymethyl Methacrylate

Thermo-forming of PMMA is entirely based upon the use of imported cast sheet.

mainly 'Perapex'. Extrusion grades of sheet do not appear to be used, although should the demand for non-illuminated display articles and signs develop, economic considerations might well bring about its acceptance on a limited scale.

Visits were made to and discussions held with :

Three sign manufacturers.

Two light fitting manufacturers.

The major import agent for 'Perapex'.

An entrepreneur who was interested in the possibility of manufacturing cast sheet.

In consequence the following tentative estimates of the CARIFTA market for cast

sheet were made :

Trinidad and Tobago	200,000 TT\$ p.a.	4,000 sheets
Jamaica	200,000	8,000
Barbados & Guyana	200,000	4,000
Other islands	<u>50,000</u>	<u>1,000</u>
	<u>700,000</u>	<u>16,000</u>

These figures are based upon the production of sheet of average thickness 1/8"

to 3/16" at 20TT\$ per 8 ft. x 4 ft. sheet. On the basis of the current use of sheet

TABLE VI

CONSUMPTION AND TRENDS IN POLYMETHACRYLATE CAST SHEET

Visit Report No.	Process	Product	General Trends	Current Usage (1971/72)		Value IT\$	Source
				Thickness range (ins)	Sizes range (ins)		
20	Vacuum forming	Signs of complex curvature.	Commenced production 1965. Limited site capacity - fully utilised.	1/8 to 1	AV. 8' x 4' some 6' x 10'	72,000	I.C.I.
	Drape forming	Simple shapes e.g. windcreens.					
	Machining	Fabricated items.		some rod			
24	Vacuum forming	Signs, exterior lighting lenses.	Recently expanded into new factory	1/8 and 3/16	8' x 4' and 10' x 6'	600 ('72) Could not say 500 ('71)	Japan (cheaper than I.C.I.)
37	Fabricated flat signs (raised letters)	Signs		Mostly 1/8	8' x 4'	325	I.C.I.
43	Blow forming (concrete moulds)	Exterior lighting lenses.	Recently lost large contract **	Mostly 1/8	6' x 4'	1,000 Av.	I.C.I.
				Total sheets --		2,925	
Perspex Agents				Mainly 1/8 and 3/16 Some 1/16 to 1/4		2,500 (Local sales) + 800 (Northern Islands)	

* Includes Methylmethacrylate glue

** Contract for street lighting lenses lost through importation of complete lights from Japan.

in Trinidad such a target could be expected to be achieved in three or four years.

Allowing for the re-use of monomer produced by depolymerizing scrap this would consume approximately 16 tons of virgin monomer per annum.

CARIRI has submitted a proposal to the entrepreneur that they undertake a complete feasibility study for such a project. The process is described in a report (4) issued by UNIDO. This report gives an excellent guide to the process but omits to include reference to the partial use of monomer produced by the depolymerization of poly-methylmethacrylate scrap, which can make a significant contribution to the viability of the process. Should such a process be undertaken it would enable other items to be cast in PMMA, such as rods, tubes, blocks etc. and facilitate the establishment of an encapsulation industry for the production of souvenirs and display items.

8.1.2.2. Expansion Plans

Sign manufacture in PMMA is considered likely to continue expanding with the smallest manufacturer shortly moving into a new I.D.C. factory and undertaking more thermoforming. Despite the loss of the lighting contract the manufacturer

concerned is confident that increasing their range of light fittings would lead to increased use of PMMA sheet.

3.1.2.3. Possible Encroachments

One sign and lighting manufacturer is considering the possibility of partially replacing PMMA by cellulose-acetobutyrate in order to obtain an advantage by purchasing in rolls. This is currently being evaluated for certain smaller lenses in the U.K. It is probably too flexible for use in display signs. While PMMA is quite satisfactory for strip lights and 25 and 250 watt bulbs, it distorts under the heat generated by 400 watt bulbs and one firm is seeking an alternative material for this application. Polycarbonate was recommended for trials and particulars of a European manufacturer given.

3.1.2.4. Artificial teeth

Some 6 tons per annum of polymethyl methacrylate dough, syrup and monomer is consumed annually in the manufacture of artificial teeth. The company is a fully

owned subsidiary, operates the process under strict control from its American parent to produce some 50,000 teeth per day. While having an 80% share of the Trinidad and Tobago market this represents only about 1% of their total market, the bulk being exported throughout the world, particularly to U.S.A., Europe, Australia and New Zealand.

3.3 Synthetic Resins

This section comprises a study of those markets in which synthetic resins are employed as ingredients in other materials, there being no indigenous manufacture of synthetic resins of any type. The object of this aspect of the survey being to establish the conditions necessary in order to assess whether the manufacture of certain types of synthetic resin would be justified.

Some twenty-four visits were made to synthetic resin users, and representative selections of manufacturers fabricating products embodying thermosetting resins in the cured state. The distribution of visits is shown in Table VII.

TABLE VII.

Distribution of Visits in the Synthetic Resin Sector

<u>Sector</u>	<u>No. of Visits</u>	<u>% of Sector</u>
Paint manufacture	4	100%
Adhesives	4	100%
Printing inks	1	100%
Foundries	1	33%
Polyurethane foams	3	100%
Automotive Assembly	1	33%
Decorative Laminate distribution	3	30% (approx.)
Fibre Board (Bagasse)	1	100%
Reinforced Plastics	4	100%
Unsaturated polyester body fillers	2	-
Furniture manufacture	1	3%
Potential raw-material manufacturers	3	-

For the purpose of assessing the feasibility of resin manufacture it was decided to

group synthetic resins according to the type of plant in which they can be most conveniently manufactured. The basis for which was decided by the author's experience and major disadvantages accruing from using possibly unsatisfactory equipment.

Group I. Alkyds and polyesters manufactured in high temperature (180°C to 200°C) jacketed vessels, normally oil or Dowtherm jacketed.

Group II. Polymer latices manufactured in steam jacketed vessels equipped for rapid cooling, efficient stirring and means for delivering liquid ingredients at controlled rates.

Group III. Aldehyde based resins, viz. phenolics and aminoplasts, manufactured in steam jacketed equipment at temperatures up to approximately 150°C, requiring efficient cooling and stirring.

While certain resins from each group can be manufactured in the equipment from another group this inevitably gives rise to problems of cleaning and cross-contamination, which in the case of polymerization products can cause partial or even complete inhibition.

3.2.1. Alkyds and Unsaturated Polyesters

3.2.1.1 Paint and Printing Ink Manufacturers Alkyd Requirements

TABLE XII

Oil Modified Alkyd Requirements

<u>Alkyd Type</u> <u>Oil Length</u>	<u>Description</u>	<u>Solids</u> <u>%</u>	<u>Solvent</u>	<u>Recent</u> <u>Growth</u> <u>% p.a.</u>	<u>Current</u> <u>Demand</u> <u>71/72 tons</u>
Medium	Linseed Glycerol	70-75	Xylene & white spirit	25 (overall)	300
Long	Soya pentaeryth- ritol	70-75	"		100
Medium	Linolenic rich linseed	"	"	Fastest growing	80
Medium & long	Linseed glycerol	-	-	6	100
-	Soya pentaeryth- ritol	-	-	"	25
-	Safflower				12
Medium & long	Linseed glycerol*	70%	W.S.	5x since 1965 (overall)	350
-	Others including soya- penta and castor oil	Var	Var		80
-	Styrenated alkyds	-	-		70
Printing inks imported ready pigmented based on alkyds					<u>24</u>
Total:					<u>1,141</u>

*Self-manufactured by fusion process in open pots. This would not inhibit purchase from a local manufacturer provided that he was not competing in paint manufacture.

In addition, the Manager of the Trinidad sales company of a large paint and resin manufacturer was interviewed. They manufacture paints for the Caribbean area in Jamaica. He was unwilling to disclose the information we required and stated that should his company decide to erect a synthetic resin plant in Trinidad they would do so without assistance from any government organization.

Imports of paint (S.I.C. 533.03.01) and varnishes (S.I.C. 533.03.02) for 1971 totalled 59,857 gallons. Assuming conservatively that 25% of this comprised alkyd vehicle, this would bring the total to a figure in the order of 1,300 tons.

The bulk of alkyds imported into Trinidad are supplied by a large Dutch manufacturer who compares favourably with other resin manufacturers, in Europe and the United States of America, in terms of price and quality. Typical prices were quoted by respondents as follows :-

Medium oil length linseed glycerol phthalate (70-75% solids in White spirit) - 33 cts. TT per lb. Assumed in lots of not less than 10 tons. Long oil length soya pentaerythritol (solids as above) - 41 cts. TT per lb. do. Raw Materials: All raw materials would have to be imported for an indefinite period as the production of even phthalic anhydride is not currently planned and by-product glycerol from soap manufacture is exported, for refining, in the crude state. A profile of alkyd manufacture is given in Appendix II.

3.2.1.2. Unsaturated Polyesters

Currently unsaturated polyester resins are being used locally in the manufacture of reinforced plastics and body fillers for automobiles.

Glass Reinforced Plastics

Although one company has been producing GRP items for a longer period than their competitors, both of whom are currently concentrating on the manufacture of power boats, they have been overtaken by them in terms of stated resin consumption. In addition to these organizations other plastics fabricators are studying the field and carrying out experimental production.

Although the current consumption of unsaturated polyesters in GRP applications is relatively small, there is little doubt that this has a potential for continued rapid expansion. It is also possible that manufacturers, on a smaller scale than those listed, have been overlooked because of time considerations. Consequently, the total given in Table 9 should be adjusted to 150 tons. All the firms listed expressed intentions to diversify by expanding their range of GRP products.

TABLE IX

UNSATURATED POLYESTER RESINS - CONSUMPTION IN REINFORCED PLASTICS

Visit Report No.	Products Manufactured	Grade of Resin	Prices cts TT per lb	General Trends	Consumption 1971/72 (tons)	Manufacturing Method
3	Chairs Corrugated Roofing Boats	85% general purpose 10% isophthalic 5% MET acid	38-40	No significant increase since 1965.* Severe space limitations. Going to new site.	20	90% by spray-up 20% hand lay-up
6	Boats	90% general purpose. 10% Gel coat	52-53	Expanded from 20 tons consumption in 1970. Expansion expected to continue at same rate.	80 ('72)	Hand lay-up converting to spray-up
17	Boats Trunks (minor)	High impact-water resistant Chemical resistant (isophthalic)		Commenced in 1969. Production expected to double again in 1973.	35 ('72)	Hand lay-up
TOTAL -- --					135	

* By comparison of figures stated with those given in report "Improvement of Plastic Processing for Export from Trinidad & Tobago" - K. Inagati to I.D.C. and Ministry of Planning.

Future plans include:

Building Products - Bagasse board filled modules for construction of recreation chalets etc. similar to those by Wight Plastics, U.K. who are using expanded PVC cores.

Public Transport - bus etc. seats.

Car bodies - have planned possible production of a GRP buggy body.

.Baths, sinks, building panels etc.

- Purpose built GRP furniture.

In the light of these considerations it is thought that resin consumption in GRP could well reach 500 tons per annum by 1975/76.

Automotive Body Fillers

The main supplier of body fillers in Trinidad & Tobago is a large paint manufacturer who distributes through a local agent. They claim to have a 75% share. While they were unwilling to disclose quantities involved, it was stated that the value of their sales amounted currently to 1,200,000 TT\$ per annum. Of their competitors they considered that the smaller firm interviewed held 4-5% of the market, the remainder being distributed between a number of smaller manufacturers. The smaller firm interviewed contended that the market distribution is :

The large paint manufacturer	70%
Themselves	10%
Others	20%

Their current sales, which have been achieved during the last two years, are in the order of 25 tons per annum. Accepting their figures, as being the most conservative, an overall consumption in the order of 250 tons per annum is probable. This would represent approximately 150 tons of resin on the assumption of an approximate 40% filler content.

As undoubtedly their use is well known to all automotive repair shops, it is probable that this market is fairly saturated and further growth limited by such factors as increase in the car population, the ability to export to CARIFTA and other countries and a possible increase in 'do-it-yourself' car repairs.

On the basis of the large paint manufacturer's figures of 1,200,000 lbs. p.a., at their current selling prices of 12 TT\$ per gallon and 4 TT\$ per quart; an average 14 TT\$ per gallon at a density of 1.2, their sales would represent approximately 450 tons p.a. of body filler and an approximate total consumption of 270 tons p.a. of resin. The current total consumption of unsaturated polyester resin is therefore in the order of from 300 to 420 tons p.a. This gives a total demand for oil modified alkyds and unsaturated polyesters in the order of from 1530 to 1730 tons.

Assuming a growth in the demand for alkyds in a conservative order of 6% p.a., the requirements by 1975/76 are likely to be in the order of from 1,970 tons to give a combined forecast of from 2,470 tons by 1975/76. Assuming an average batch production time of 10 hours, including down time for cleaning etc., and a working year of 6,000 hours (50 x 5 days, 3 shifts), this would represent 80% capacity for one 1,000 gallon or two 500 gallon kettles.

3.2.2 Synthetic Latices

Particular attention is given in this section to polymer latices based upon monomers which are capable of being reacted at ambient pressure. Those latices embodying gaseous monomers are produced by a more limited range of manufacturers, frequently by continuous processes.

Of major importance in this sector are polyvinyl acetate and vinyl acetate co-polymers, both types being utilised mainly in the manufacture of surface coatings and adhesives.

TABLE X

Latex Type & Solids	Application	General Trends	Consumption	30
			1971/72 (tons)	Prices
Vac-vinyl versamate* 55%	Surface Coatings	Rapid expansion	300	
PVAC 55%		Since 1965	110	
PVAC - high viscosity) PVAC - low viscosity) VAC flexible copolymer)	Adhesives	more than trebled since 1968. Growth rate maintaining	100('71)	
PVAC in various viscosity grades	"	commenced 1969	60('71)	50-100¢/TT F.O.B.
PVAC	"	packaging only	10('71)	
VAC-ethylhexyl acetate copolymer	" press sensitive	minor quantities only	-----	
TOTAL:			580 tons	

Notes: One surface coating manufacturer and one adhesive manufacturer use styrene-butadiene latices, the former as an alternative to PVAC.

* This manufacturer is evaluating vinyl acetate-ethylhexyl acrylate copolymer latex as an alternative to vinyl acetate-vinyl versamate copolymer.

Acrylics

A variety of copolymers of acrylates and methacrylates are currently being used on a rapidly expanding scale in the surface coatings field, particularly in automotive finishes. They

feature such properties as:

Tailored properties which respect of flexibility and curability

Water solubility for electrophoretic application.

They may be produced as latices or in solution. Certain grades may also be incorporated into polishes. Although currently their use by local manufacturers is small growth may be likely to accelerate in the future. Current usage by respondents amounts to some 25 tons. They would be capable of manufacture in similar equipment to that used for synthetic latices. The use of synthetic latices is expanding more rapidly than that of alkyds and should reach the 1,000 tons per annum mark within the next five years. Consideration should therefore be given to indigenous production, possibly on a lower priority than that of alkyds and unsaturated polyesters.

During the survey we were informed that two separate surveys into this field have been carried out by U.K. resin manufacturers.

3.2.3. Aldehyde Condensation Products

The applications for resins of this class are distributed over a wide range of industrial sectors. They may function, in the cured state, as binders in a variety of manufactured products including:

Abrasive products such as grinding wheels.

Friction materials, including brake linings and clutch facings.

Industrial and decorative laminates and bushings.

Automotive filters and battery separators.

Thermoset mouldings, via moulding powders as yet not manufactured here.

They may, if necessary, be compounded with other ingredients and sold in the uncured state to manufacturers in such industrial sectors as:

Foundries, as sand binders.

Adhesives manufacturers, for packaging and use per se, or as modifiers for other adhesives, e.g. synthetic rubber cements and sealing compounds lamp capping cements etc.

Pulp and paper manufacturers as binders, wet strength additives and impregnants.

Textile manufacturers and dressings, shrink resistant and crease resistant additives.

Polish manufacturers as gloss and hardening agents.

Rubber products manufacturers as reinforcing and hardening agents etc.

In the former class such manufacturing industries have yet to be established in Trinidad and Tobago prior to any demand for resin, but the Industrial Development Council have prepared industrial profiles on abrasive products and friction materials which will be assessed later in this report. In view of the extensive use of decorative laminates in the furniture and other sectors an attempt has been made to assess demand in order to obtain indications of the likely viability of indigenous manufacture and of paper impregnation and coating which could potentially facilitate the manufacture of automotive filters and battery separators. In this class the viability of manufacture of this type of resin may well hinge on the success of the bagasse board project which is about to go 'on stream', this is also reviewed later in this report.

TABLE XI

CONSUMPTION OF ALDEHYDE RESINS BY ADHESIVES AND SURFACE COATINGS MANUFACTURERS

Visit Report No.	Application	Resin Ingredient	Consumption General Trends	1971/72 (tons)
15	Stoving finishes	Butylated aminoplasts		10
	Marine varnishes	Substituted phenolics i.e. -p-t-butyl or octyl phenol resoles		8
2	-do-	-do-		10-15
5	Neoprene cements	-do-	Good growth for bonding decorative laminates	8-10
	Wood adhesives (furniture)	Spray dried U-F	Steady growth	60
11	Neoprene cements	Substituted phenolics	-	1/4
	Rubber reinforcing (ply adhesion)	C.N.S.L. modified phenolic		4-1 1/2
12	Wood adhesives	Spray-dried U-F	Increasing	Est'd 20
	-do-	Liquid phenolic (hot or cold curing)		12
22	Neoprene cements	Substituted phenolics embodied in imported adhesive	-	10
			TOTAL -- --	130 to 146 tons

In the latter class the following contributing factors were ascertained :

1. Foundries: The foundry manager interviewed confirmed that his organization also functioned as the distributor of products for a large foundry products manufacturer and that none of the three foundries on the island use synthetic resin binders. His foundry and to a lesser extent the others had adopted the CO₂ process involving the use of sodium silicate as binder.
2. Pulp and Paper: No paper mills exist as yet. Tentative enquiries have been made of CARIRI with respect to establishing a manufacturing process for pulp moulded egg trays, from scrap newsprint. This project could ultimately involve the use of a urea-formaldehyde binder.
3. Textiles: Although there is a well established garment industry no weaving is carried out.
4. Adhesive and surface coatings manufacturers were visited and their use of aldehyde resins is given in Table II.
5. Polishes. It was understood that although polishes of all types are imported none are indigenously manufactured. In any event formaldehyde resins, in particular substituted phenol resoles, are only used in minor proportions.
6. Minor quantities of rubber reinforcing phenolics are being used in the manufacture of radial ply tyres, viz up to only 1½ tons per annum. No visit was made to the other rubber manufacturer.

In consequence of these findings it becomes obvious that the manufacture of aldehyde resins should be put on a lower priority than those in the other groups, unless such manufacture is preceded by the establishment of a relatively large capacity process, such as bagasse board and/or decorative laminates.

3.2.3.2. Binder Requirements for Bagasse Board

The bagasse board plant is scheduled to go 'on stream' in August 1972. It is designed to produce 36 tons per day (10,000 tons per annum) by the end of 1973, in accordance with the following target schedule:

August, 1972 to January 1973	- 1 shift per day
January 1973 to June 1973	- 2 shifts per day
June/July 1973	- 3 shifts per day for 280 stream days per annum.

It is further anticipated that its capacity will be expanded to 48 tons per day, possibly within two to three years.

For general purpose boards the binder will consist of a spray dried urea-formaldehyde resin to the following specifications :

Specific gravity at 20°C.	1.20 ± 0.05
Viscosity at 20°C.	200 to 8,000 cps. at 50% solids.
pH	7.5 ± 0.5
Free formaldehyde	1.0 ± 0.5%
Cure	Conventional ammonium chloride hardener.

For special purpose, moisture resistant grades, the binder will consist of a liquid phenol-formaldehyde resole.

With an average binder content of $9\frac{1}{2}\%$, the distribution of general purpose to special purpose boards is expected to be in the order of 90 : 10.

Although the project is based upon the use of imported resins it is understood that, once established, preference would be given to the use of indigenously produced resins. Should this be achieved the use of spray-dried resin could be modified to a liquid Urea-formaldehyde resin to eliminate the re-constitution step.

With a binder distribution, based upon bone dry bagasse weight, of 9.8% for the outer layers and 8.6% for the core, binder requirements for 10,000 tons of board per annum would be 1,400 tons of liquid resin at 60% solids content per annum.

A single resin kettle of 500 gallons capacity would be capable of producing about 5 tons per day of the types of resin binders used, on a three shift basis. Thus it could be expected to comfortably accommodate the quantities envisaged, with probably sufficient space capacity to produce for other outlets. In order to maintain flexibility, however, it would be undesirable to base such a resin unit on a single kettle. It is most probable therefore that additionally a smaller kettle, of for example, 250 gallons capacity should also be installed.

Board pressing is based upon the use of a four daylight $13\frac{1}{2} \times 6$ ft. hydraulic press, in addition to which a single daylight veneering press has been installed. Operating pressures are in the order of 130 p. s. l. (10 kg/sq. cm.), which are insufficient for the production of decorative laminates, but marginally adequate for in situ facing with resin pre-impregnated decorative surface papers.

3.3.3.3. Decorative Laminates

In view of the apparently extensive use of decorative laminates in Trinidad and Tobago, it was decided to undertake a preliminary assessment of this market.

Laminates are principally used in facing the cheaper quality furniture and kitchen furniture. It is purchased both by furniture manufacturers and also, through wholesale and retail hardware stores, by the public. Most of the island's 57 furniture manufacturers obtain it through a number of importing agents ranging from the importers of well known brands; including 'Formica', 'Arborite' and 'Wareite'; through to an indefinite number of agents factoring cheaper qualities imported from countries throughout the world. From the survey it is apparent that the more expensive established brands have suffered a significant decline in favour of cheaper materials. Current imports and their trends are given in Table 12.

Consideration is being given to manufacture locally by two importing organisations, the possible the first on acquisition of a redundant 8' x 4' press instituted a market survey from which he was unable to draw conclusions as to the overall size of the market and

TABLE XII

DECORATIVE LAMINATES - SUMMARY OF VISIT REPORTS

Visit Report No.	Type of Organization	Brand Name(s) or Sources	Dimensions		General Trends	Annual Sheets (sq. ft.)	Turn-over year
			Superficial ft x ft	Thickness			
16	Furniture and PU foam manufacturer (medium sized)	From W. Germany, Brazil etc.	8 x 4	1/16"	Continued expansion	92,000	1971/72
30	Import agent	"Laminite" (Canada)	8 x 4	0.8 mm 1.0 mm * 1.2 mm 1.5 mm	Started 1969, abandoned 1970, resumed April 1971.	590,000 1 to 1.4 million.	4/71 to 4/72 1972 (Pred)
33	Importer	'Arborite' (Canada)	up to 12 x 5	Various mainly 1 mm	Current demand static	273,000 270,000 270,000+	1970 1971 1972 Pr (Pred)
Tel.	Importer	'Formica'	10 x 4	mainly 1 mm	Current demand static	240,000 to } 320,000 } (Pred)	1972 (Pred)

* Most popular thickness

its degree of saturation. The second on the basis of a package deal including know-how, including two impregnating machines and starting from imported raw papers and resins. The justification for this approach including an assessment of the current overall Trinidad and Tobago market as being in the order of 2 million square feet of laminate per annum, and that export to the Caribbean and world markets was achievable. In the author's opinion, while it may be natural to minimise investment capital by importing pre-impregnated paper and confining the process to laminating trimming and sanding only, it is possible that if impregnation equipment were installed it would lead to a greater potential for diversification into other lines involving impregnated and coated papers and fabrics. With regard to the package deal, described above, the use of two impregnators, for separate impregnation of phenolic and melamine-formaldehyde papers, appears to be an unnecessary luxury.

3.2.3.4. Automotive Filters and Battery Separators

Both automotive filters and certain battery separators are based upon phenolic

impregnated porous papers. In the latter instance the Island's largest battery manufacturer stated that they used no paper separators but were committed to using PVC separators, of both the sintered type and the starch expanded type, by their principals because of their superiority under tropical conditions.

Having been approached by a client, interested in manufacturing air, fuel and oil filters as replacements for commercial and private vehicles, CARIRI are currently investigating the possibility of acquiring information as to package deals involving know-how and plant for production based upon imported pre-impregnated paper.

3.3 Miscellaneous plastics and resins

In addition to the items dealt with in sections 3.1 and 3.2 of this report there is an active growth in various polyurethane products, particularly foams for upholstery and insulation and polyurethanes for surface coatings. Also CARIRI has become involved in a number of projects involving such polymers as Lake Asphalt and the polymerization of crude oil, on which the author's advice was sought.

3.3.1. Polyurethane Foams

Two organizations are manufacturing flexible polyurethane foam blocks and mattresses. Both are using polyethers obtained from America and using combinations of TDI, tertiary amines and water for simultaneous foaming and curing. Their combined resin usage currently amounts to less than 400 tons per annum but one of them only started production in February of this year. Experimental production of rigid polyether foams is being investigated by two companies.

3.3.2. Polyurethane Surface Coatings

It is anticipated by one manufacturer that his demand for polyurethane modified safflower oil for varnish manufacture in 1972 will be in the order of 17 tons and another manufacturer imports a similar product in the form of the varnish. A high growth rate for these products is expected, possibly at the expense of varnishes based upon substituted phenolic - tung oil. Should, at a later stage, quantities be sufficient to justify manufacture it is anticipated that they could be made in the alkyd plant.

3.3.3. Expanded Uses for Lake Asphalt

The Industrial Development Corporation had requested advice from CARIRI on additional fields of application for Lake Asphalt in view of possible declining use in road surfacing. It was agreed to concentrate upon those aspects of its properties which differed significantly from those of oil and coal bitumens. The following proposals were made and actions taken :

1. In view of the high mineral content of Lake Asphalt and the expense of its removal, investigation should be limited to those fields in which it was acceptable.

2. In the light of recent developments in sulphur polymers and their use, particularly in the building of low cost houses, coupled with the future availability of sulphur from local oil de-sulphurization plant, attention should be given to possible asphalt-sulphur combinations. The author was aware of general work in this field and was able to obtain further bibliographical information from the following :

Dr. Currell, the Polytechnic of North London
The Sulphur Institute, Washington, D.C.
Shell (Canada) Ltd.

3.3.4. The Polymerization of Crude Oil

A local entrepreneur had acquired the rights to a new process for the rapid manufacture of a variety of materials, ranging from foams to moulded solids, by modification of crude oil by undisclosed resinous products; presumed by the author to be along the lines of isocyanate terminated polyurethanes. CARIRI had been requested by I.D.C. to comment upon the genuineness of the process.

During discussions with the entrepreneur it became apparent that his U.K. patent agent was a client of the author. The author had conducted a prior art search of U.K. patents in this field during late 1971 and obtained a copy of his report for CARIRI. This document also contains items of possible relevance to 3.3.2. above.

3.3.5. Industrial Development Corporation - Industrial Profiles

3.3.5.1. Brake Lining Manufacture (Industrial Profile No. 10).

With the desire to increase the local content of automobiles, in which already includes replacement tyres and batteries and will include them as initial equipment

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from July and January 1973 respectively, it is natural that the possibility of manufacture of other component items be promoted. With this in mind the I.D.C. issued an industrial profile. This was based upon the premise that, for replacement demand brakes are re-lined at approximately four month intervals for both private and commercial vehicles, giving an annual demand for 500,000 sets for a car population of 100,000. In the author's opinion a more realistic figure was given by a large automotive assembler, using some 30 different sizes of linings including conventional moulded linings and discs, who estimated that the life of a lining averaged out at approximately two years. This reduces the current replacement demand to approximately 75,000 sets, for the local market.

In the light of the critical nature of brake linings and the need for thorough evaluation and testing of all constituents and finished linings, such a project would need to be undertaken by an established brake lining manufacturer who would no doubt also manufacture clutch facings in similar plant. In order to be viable the factory would need to cater for a much larger market than Trinidad and Tobago alone.

As a minimum requirement it would be strongly advisable to make a prior assessment

ment of the viable area to be supplied and whether or not manufacture would need to be restricted to selected sizes and types of linings.

3.3.5.2. Abrasive Cloths and Papers (Industry Sheet No. 6)

From the aspect of synthetic resin consumption the requirements in this field are very small including only minor additions of phenolics and aminoplasts as hardeners for animal glue and possibly alkyds for specialised grades of water-proof abrasive cloths. Larger quantities of synthetics, particularly phenolics, are used in the manufacture of grinding wheels and cutting discs.

3.4. Raw Materials

Although the advantage of using indigenously produced raw- materials is obvious, these are extremely limited and plans for the extension of the range somewhat remote at this juncture.

In the Government of Trinidad and Tobago's Five Year Plan (1969 - 1973) the possibility of establishing a petrochemical complex is discussed (4). It is

TABLE XIII

COMPARISON OF LOCAL CONSUMPTION OF RAW MATERIALS WITH MINIMUM VIABILITY OF THOSE OUTLINED IN THE NATIONAL PLAN

Petrochemical Basis	Products	Category	Form used currently	Quantity (tons p.a.)	Approx. material content (Av.)	Amount (tons p.a.)	Min. viable production (tons p.a.)
Naphtha (steam cracking)	PVC	A	Moulding & extrusion compounds (excl. co-polymer)	1,145	70%	800	20,000
-do-	Polystyrene	A	Moulding & extrusion compounds and H.I. sheet				
-do-	{ Polythene-LD Polythene-HD }	A	Moulding & extrusion compounds	1,250	99%	1,250	50,000
-do-	Phenol	B	Negligible	750	99%	750	20,000
Benzene, toluene etc.	Polystyrene	A	Moulding & extrusion compounds and H.I. sheet				
	Formaldehyde	B	P-F and U-F	App. 1,000 *	50% in uncured resin (dimethylol urea)	1,330 (at 37.5%)	20,000
Xylene	Phthalic anhydride	B	U.M. Alkyds and unsaturated polyesters	1,300 App. 500	24% 36%	312 190 502	10,000
Propylene	Polypropylene	A	Moulding & extrusion compounds monofilament and yarn	160	99%	160	10,000

NOTES *Requirements of the bagasse board plant, when operating to capacity. The quantities given in Column 7 do not include amounts contained in imported films fibres and finished goods.

recognized that the establishment of such a complex would be dependent upon access to markets outside CARIFTA. Should such a complex be established it is clear that the proportions of materials produced utilised in indigenous plastics processes would be of a low order. These might conceivably selected from the following groups outlined in the Plan according to which group was selected. In order to give an indication of perspective an order of the amount of polymer or intermediate currently utilised (Category A) or required in the event of resin plant being installed to meet import substitution requirements (Category B) is compared with the probable capacity of a minimum viable sized plant, in Table XIII.

Prilled urea is produced by Federation Chemicals Ltd. Although primarily a fertilizer grade, its quality is adequate for the production of Urea-formaldehyde resins for the bagasse project and other outlets. It is manufactured to the following

specifications:

	<u>Limits</u>	<u>Normally Achieved</u>
Total Nitrogen	46.6% Min.	
Moisture Content	0.5% Max.	0.35
Biuret	1.5% Max.	1.3%
Free Ammonia (NH ₃)	150 ppm.	
Ash	35 ppm.	
Iron	1.5 ppm.	
Oil	5.0 ppm.	1.0 ppm.
Colour - Alpha Scale	3	
Turbidity (SiO ₂)	7.0 ppm.	
pH	7.0 to 9.8	
Screen Size (U. S. Mesh)	Passing 6 - 100% retained by 20 - more than 90%.	

To produce 1,000 tons of medium oil length alkylid approximately 130 tons of glycerol is required. Although one of the local soap manufacturers produces approximately 200 tons of crude (80%) glycerol per annum as a byproduct, the amount is considered too small to justify refining and it is exported to Venezuela. In the crude state it is quite unsuitable for alkylid manufacture. Refined glycerol is imported, 54 cts TT per lb., for use in toiletry products etc.

Of particular interest to the author is Cashew Nut Shell Liquid, an unsaturated phenolic material, which has quite wide usage in the industrial resins field. Apart from cashew trees being of common occurrence on the island, there is one small plantation on the slopes of Mount St. Benedict. The possibility of more extensive cultivation in order to produce exportable quantities of kernels, and shell liquid has been dealt with in a Report, the conclusions of which appear somewhat nebulous. Owing to lack of time, however, this subject was not pursued.

3.6. Training in Plastic Technology

In all respondents interviewed in the thermoplastics conversion sector, it was

stated that training for a particular process had been given either by their parent company, the plant manufacturer or the polymer manufacturer, and was substantially confined to the particular operations involved in the specific conversion process.

Particularly among the more senior executives this was supplemented by visits to major plastics exhibitions and attendance at courses overseas. While agreeing that, largely because of pressure of work, the support for formal courses covering the whole field of the technology, would most likely be inadequate, most respondents thought that there was a need to expand the range of their knowledge of the plastic field. It was generally considered that this could best be met by attendance at periodic symposia or seminars on selected topics.

With this in mind a trial one day symposium was organized, the programme for which is included in Appendix III .

The Symposium, held on July 14, was attended by some 70 delegates drawn from: local industry, staff and students from the University of the West Indies and representatives of the engineering profession, architects and the Fire Service.

A small exhibition, held simultaneously, in the reception area comprised a selection of locally made plastics products, and representative trade literature from the larger raw-materials suppliers. Lists of CARIRI holdings of textbooks, journals and monographs relevant to plastics technology, together with the Plastics Institute's list of monographs, were available for distribution. As a first symposium of its type it was considered by both the organizers and delegates to have been highly successful. The discussion periods, including the 'Open Forum', were recorded on tape and copies of the full papers obtained by CARIRI.

As an introduction to plastics technology for the initial benefit of CARIRI staff, the author presented a one half day seminar. The papers were subsequently written up for presentation to CARIRI staff and delegates to the one day symposium. This document comprises Appendix V.

The following training programmes organized by UNIDO and other bodies were discussed:

'Symposium on Plastics Fabrication in Latin America', Bogota. 20 November to 1 December 1972. - United Nations.

'Plastics Training Programme', Vienna, 4 September to 3 November 1972. United Nations.

Training Seminars: New York University. A series of 11 separate five day symposia, each dealing with a specific aspect of plastics technology, and being repeated at least twice, has been organized to run throughout 1972.

• **At present there is no member of CARIRI staff experienced in Plastics**

• **Technology.** It was, however, considered that representation at the Symposium

1. would be beneficial, consequently application was made for one of the Expert's

counterparts, Mr. Gary N. Voss, to attend. Owing both to pressure of work and

the proximity of the Plastics Training Programme 2. it was decided not to apply

for representation. Training seminars of the Type 3. would be more advantageous

when CARIRI had an appropriate member of staff concentrating on Plastics Technology.

4.0 DISCUSSIONS AND RECOMMENDATIONS

4.1 THERMOPLASTICS CONVERSION

4.1.1 Discussion

Among the thermoplastics converters a very dynamic situation exists. Almost without exception they have disclosed plans for further expansion and diversification into additional lines and conversion processes. Although in most cases manufacture is severely restricted by the size of the local market and the limitations imposed on exports by the existence of similar processes within the CARIFTA and other nearby countries.

Conversion processes are, of necessity, on a significantly smaller scale of operation than those of the developed countries having very much larger local markets.

The size of the local market at a population of 1,100,000 is such that a single organization and, in extreme cases, a single plant item or even a mould can cater for a far larger market.

Thus where high capital costs are involved, such as imported moulds for injection and compression moulding, they may constitute a marked economic imbalance.

No example of compression or transfer moulding of thermosetting moulding powders was found but one organization announced the intention of producing specialised electrical grade mouldings from such materials.

In a number of cases inadequate attention appeared to have been paid to market considerations prior to investment in plant. The possibility of overcapacity for a particular item, arising from uncoordinated decisions to produce it by more than one organization could create future difficulties.

No heavy duty compounding equipment for thermoplastics was located, other than a recently installed Henschel Mixer. It is most likely that the demand for extrusion and moulding compounds in relation to the number of different compounds involved would not justify the high investment needed to set up a separate compounding organization at this

junction. The extruders who have acquired the Heuschel Mixer have, however, planned to link this with an extruder-mixer and, after having fulfilled their own requirements for compound, consider offering a compounding facility to other organizations. Currently most of the converters purchase their compounds from the larger polymer manufacturers, such as I.C.I. and Hoechst, thereby obtaining materials of more consistent quality than would be attainable from a trade compounder, particularly during his early stages of operation.

The growth of the local consumption of cast polymethyl methacrylate sheet for signs and lighting fittings should continue. The estimates of the current demand for the CARIFTA countries is approximately 5000,000 sq. ft. per annum. This potential market should justify a more detailed study with a view to establishing an indigenous casting operation. Thus the opportunity for CARIRI to undertake a feasibility study on behalf of a client organization should be pursued.

4.1.2 RECOMMENDATIONS

4.1.2.1 As the existing thermoplastics converters have already announced plans for expansion and diversification and a number of other organizations have also announced intentions or ordered plant for conversion it is recommended that expansion in this field, at this stage, is left to them.

4.1.2.2 The formation of a Trade Association or similar body, to coordinate this sector of the industry and exploit to the maximum such activities as mould hiring schemes, dissemination of information regarding plant capacities and the avoidance of duplication in manufacture, is recommended.

4.1.2.3 The feasibility of establishing a plant for the manufacture of cast polymethyl methacrylate sheet should be studied in detail in the light of process described in

4.1.3 the United Nations Monograph No. 6. (3), possibly modified by the inclusion of a means for preparing part of the monomer feed from depolymerized scrap.

4.2 SYNTHETIC RESINS

4.2.1 Discussion

The current demand for oil modified alkyd resins, by surface coatings manufacturers, coupled with the current demand and future growth potential of unsaturated polyesters strongly indicates a need to consider indigenous manufacture of these resins. They can be conveniently manufactured in the same equipment which would basically comprise:

i. A high temperature (250° to 300° C.) jacketed reaction vessel, preferably in stainless steel. Which may be oil or Dowtherm jacketed or induction heated. Equipped with:

- i. Condenser adaptable for reflux and distillation.
- ii. Wide inlet to condenser.
- iii. Slow speed (app. 120 r.p.m.) stirrer - anchor type.
- iv. Immersion cooling coils.
- v. Temperature recorder.
- vi. Charging manhold.
- vii. Inert gas line to proximity of base of vessel.
- ix. Bottom discharge valve (flush seated).
- x. Bursting disc.
- xi. Valves, sight glasses, receiver, etc.

And optionally:

- i. A separator for azeotropic distillation.
- ii. A vacuum pump.

Should the reaction vessel be of 1,000 gallons capacity it would be capable of producing anticipated local requirements at least up to 1975/76, on a three shift basis. From the aspect of flexibility, however, and reduction in possible hold-ups, a unit based upon two smaller reaction vessels is preferred.

Synthetic polymer latices, in particular polyvinyl acetate and vinyl acetate copolymers, are expanding more rapidly than oil modified alkyds and their local consumption could reach the 1,000 tons per annum mark within the next five years. Assuming an average batch time of five to six hours, including cleaning and a batch yield of $1\frac{1}{2}$ tons, a 500 gallon reaction vessel could be expected to produce up to 1,000 tons per annum on a twenty-four hour shift basis.

A similar reaction vessel would also be satisfactory for the production of acrylic latices and solution polymers, which are assuming increasing importance in such fields as automotive finishes and polishes.

The essential requirements of a suitable reaction vessel include:

- i. Facilities for steam heating and rapid efficient cooling.
- ii. Efficient stirring, possibly at two speeds (120 and 250 r. p. m.).
- iii. Facilities for continuous, gradual addition of liquid ingredients (monomer and catalyst solution) after the onset of polymerization.
- iv. Efficient reflux condensation.
- v. Optional facilities for vacuum removal of residual monomer.

The applications for aldehyde condensation products particularly phenol-formaldehyde and urea-formaldehyde are distributed over a wide range of industrial sectors which include the manufacture of finished products in which they are cured as binders. Thus their market is, to a great extent, determined by the existence of appropriate manufacturing units. For this reason the decision whether or not to encourage their indigenous manufacture could initially hinge on the success of the bagasse board project. Ultimately, a resin demand could arise from products derived from impregnated papers which, should schemes for the indigenous manufacture of decorative laminates and automotive filters prove viable, could be initially produced from imported pre-impregnated papers. Such products would create a potential demand for both phenol-formaldehyde and melamine-formaldehyde resins.

At this juncture it is considered premature to consider the manufacture of the basic intermediate polyethers for polyurethane foam production as, not only are the quantities used less than 400 tons per annum but they are produced on large scale by a limited number of manufacturers in the developed countries. Should there be a reversion in the declining popularity of polyester resins as a basis for polyurethane foams they could conveniently be manufactured in the alkyd plant.

The demand for polyurethanes for surface coating applications, although currently small in Trinidad and Tobago, is expected to rise appreciably. Those based upon polyurethane modified drying oils could also be manufactured in alkyd plant.

In anticipation of the increasing availability of sulphur from the oil desulphurization plant, which is at present being constructed, and the concurrent need to extend the applications of lake asphalt it is recommended that attention is given to possible combinations of these products on an exploratory basis.

The possibility of manufacturing solid polymers and foams containing reaction products of crude oil cannot be assessed until the assignee has obtained adequate patent cover and is prepared to disclose his process. Although some of its applications may appear to be exaggerated, it may well turn out to be an exciting development.

The industrial profiles, for the manufacture of brake linings and abrasive cloths and papers, prepared by the Industrial Development Corporation, indicate the need for a more detailed assessment of technical entailment to be made prior to, or during the course of, the preparation of such documents.

4.2.2 Recommendations

- 4.2.2.1** A detailed feasibility study should be made of the desirability to establish a synthetic resin manufacturing unit (or units) for the manufacture of:

- a. Oil modified alkyd resins and unsaturated polyester resins.
- b. Polymer latices, particularly those based upon polyvinylacetate and vinyl acetate copolymers.

4.2.2.2 Prior to considering the possibility of manufacturing phenolic and aminoplast resins the following processes should be established:

- a. Manufacture of bagasse board in such quantity as would entail the use of not less than 1,000 tons per annum of binder resin.
- b. The manufacture of such thermosetting resin conversion products as decorative laminates and automotive filters, initially based upon pre-impregnated papers.

4.2.2.3 In respect of 4.2.2.2 b. Feasibility studies on the manufacture of decorative laminates and automotive filters should be undertaken.

4.2.2.4 If the results of the items in 4.2.2.3 are positive the feasibility of establishing a paper and fabric impregnating unit should be studied.

4.3 THE ROLE OF CARIRI

Although it is appreciated that the terms of reference of the Expert are confined to the field of Plastics Technology in the light of his broad experience of Research and Development extending to other aspects of the chemical industry, it is inevitable that certain comments may have more general application.

It is proposed to discuss the role of the Caribbean Industrial Research Institute under the following headings:

Industrial Promotion and Training.

Testing.

Information Services.

Staffing.

1.3.1 Industrial Promotion and Training

During its two years of existence CARIRI's name and reputation have developed and it is now well known through Trinidad and Tobago industry. Its relations with other Government bodies are well established but, in the expert's opinion, it is possible that more extensive use could be made of its technical expertise. For example a number of specific projects have been executed by CARIRI for the Industrial Development Corporation, I.D.C., but as the staff of I.D.C. are mainly economists it is probable that they could make more general use of the technical background of CARIRI staff, particularly when drawing up Industrial Profiles and executing Feasibility and Pre-feasibility studies.

A stronger liaison with Technical Colleges, both from the aspect of possible future staffing of CARIRI and in pinpointing the need for particular types of technicians and craftsmen, would be desirable.

The consensus of opinion among respondents, with regard to training in Plastics Technology, was that, at this stage there would not be adequate support for formal courses but periodic symposia would be supported, in order to broaden knowledge of the subject and promote inter-course between workers in this sector. With the facilities available on the University Campus and the relationship between CARIRI and various faculties of the University, CARIRI should be well placed to organize symposia of this type. It was with these considerations in mind that the Symposium on Plastics Technology was arranged. Involvement in the organization of such functions should also serve the purpose of promoting CARIRI within industry.

4.3.1.8 Testing

Since its inception CARIRI has progressively acquired a broad range of equipment for undertaking mechanical, chemical and physical testing and one of its functions is to offer this service to industry. Parallel to this situation it is understood that a Bureau of Standards is shortly to be established. There is little doubt that CARIRI is in an excellent position to make an effective contribution in this respect, while at the same time avoiding duplication of services.

Within the plastics sector of industry testing is greatly influenced by the following considerations:

- i. **Test schedules, particularly for products for use in technically demanding operations, are normally ordained by appropriate published standards set out in national or international specifications. The most commonly applied specifications in Trinidad and Tobago are those of the British Standards Institution and the American Society of Testing Materials.**
- ii. **Largely because of the scale of operations in relation to market size and the high incidence of affiliation with larger overseas organizations, it is common practice for most if not all of the more sophisticated testing of finished products to be carried out by the overseas organization.**

While the advantage of having local facilities for carrying out comprehensive testing schedules is obvious, in most cases the use of this facility would require approval by both the local firm and its overseas affiliate. With independent organizations, which generally operate on a smaller scale than those with overseas affiliates, there is a greater freedom of choice and CARIRI's services should be of greater immediate benefit. In assisting and promoting new operations, in particular, it is recognised that promotion of quality control standards is one of CARIRI's functions.

In predicting those sectors of the plastics industry most likely to call upon CARIRI's testing facilities, those sectors in which technically demanding products are likely to be manufactured by organizations having little formal technical orientation are likely to dominate. These include reinforced plastics, insulants based on foamed products and adhesives. Of possible particular importance may be the bagasse board development in which it is important that CARIRI should be in a position to assist by carrying out the necessary evaluation test schedules during scaling-up operations and in collaborating in the more routine quality control procedures.

3.1.3 Information Services

The potential importance of CARIRI's library and information services cannot be overstressed. One of the major difficulties experienced in the developing countries is that of disseminating and retrieval of technological information, particularly that contained in technological journals and patent literature which are unlikely to be housed in university libraries. In the long term CARIRI's information services could be regarded as a possible nucleus for a national technological library. While appreciating that such a matter would involve high policy decisions, the need for such an organization is, in the expert's opinion, self-evident.

Advice has been given on extending the library's holding of plastics journals, monographs particularly suitable for reference and training, and annually bound reviews, covering a wide range of topics in applied chemistry, which are particularly useful as a source of prior art and retrospective information. The classification and indexing of British Patent Specifications has been discussed and suggestions made in accordance with the recommendations given below.

4.3.1.4 Staffing

Currently CARIRI lacks suitable staff having experience in the plastics field. With the probable continuing high growth of such sectors as reinforced plastics and thermoplastics conversion and implementation of the feasibility studies recommended by the expert it should be anticipated that the demands on CARIRI are likely to increase in this field. A suitably experienced industrial chemist would also be able to make a significant contribution towards other, non-plastics projects.

4.3.2 Recommendations

4.3.2.1 Promotion and Training

CARIRI should maintain its efforts in strengthening its liaison with Technical Colleges, industry, the Industrial Development Corporation and other governmental organizations promoting small industries in order to maximise the use of its technical services. Until the demand justifies the organization of formal courses in Plastics Technology CARIRI should either organize, or collaborate in the organization of, periodic symposia in Plastics Technology.

4.3.2.2 Testing

CARIRI should acquire copies of all British Standard Specifications and American Society for Testing Materials specifications relevant to the plastics sector and review its test equipment items to ascertain their suitability and limitations. Additional equipment could then be considered according to likely demand and the shortcomings of their present range.

4.3.2.3 Information Services

CARIRI should extend its patent information services by:

Acquiring the Keyword (1 volume) and Classified Indices (3 volumes) of United Kingdom Patents.

This should be followed by the acquisition of selected Classified Abridgement volumes in the plastics and other fields.

4.3.2.4 Staffing

CARIRI should engage the services of an industrial chemist, who possesses experience in the production and application of plastics and capable, at least after initial support from a short term United Nations expert, of undertaking technical projects in the plastics field and carrying out feasibility studies.

4.4

FURTHER UNITED NATIONS ASSISTANCE

It is recommended that further, short term assistance be given to CARIRI and the Government of Trinidad and Tobago, in the form of a short term expert in Plastics Technology, in order to carry out the following functions:

- i. Link up with and give initial training to the industrial chemist, who it is recommended that CARIRI engage and who would function, inter alia, as the expert's counterpart.
- ii. Carry out such feasibility studies, recommended in this report, as had not been undertaken by CARIRI as specific projects, during the interim period.
- iii. Study the market, production and demand situation with respect to cast acrylic sheets, aldehyde resins, vinyl polymer emulsions, decorative laminates and other products derived from synthetic resin, impregnated and coated papers and fabrics in the CARIFTA area.
- iv. Assist CARIRI in the organization of a further symposium or seminar in Plastics Technology as a follow-up to the symposium held on 14 July 1972.
- v. Investigate the potential for indigenous Cashew Nut Shell liquid and its related and conversion products.

4.4.1 JOB DESCRIPTION

Post Title	Consultant in Plastics Technology.
Duration	Four months with possibility of extension.
Date Required	As soon as possible.
Duty Station	St. Augustine, Trinidad, with possible travel within country and other Caribbean islands producing plastics and/or their conversion products.
Duties	The expert will cooperate with and assist in the initial training of local counterpart staff in carrying out economic feasibility studies in selected sectors of the plastics producing and conversion industries, with a view to making a detailed assessment of the potential for their initiation or expansion. The consultant will also be expected to assist in the organization of a symposium on Plastics Technology to which local industrial organizations, University staff and students, and professional organizations will be invited to attend and subscribe papers. The selected sectors of the Plastics Industry will include the manufacture of alkyd resins; particularly oil modified alkyds and unsaturated polyester resins; expansion of the glass fibre reinforced plastics sector, the manufacture of cast methyl methacrylate sheet and other related products, vinyl polymer latices and acrylic

emulsion and solution polymers, decorative laminates and other aldehyde resin conversion products, particularly those derived from impregnated and coated papers and fabrics; the possibility of utilizing cashew nut shell liquid and/or its conversion products/ from local sources. The consultant will, in particular be expected to:

1. Complete detailed market studies in the sectors listed above, both with respect to Trinidad & Tobago and other countries within and adjacent to the CARIFTA area.
2. Prepare detailed surveys of process economics, investment required, site requirements and facilities, labour requirements, laboratory and testing requirements in carrying out the feasibility studies.
3. Contribute to the promotion of CARIRI within the plastics industry recommending any additional facilities needed to facilitate CARIRI's services to the industry.

Qualifications

University degree in Chemistry with extensive industrial experience at a senior level in plastics technology with particular reference to the manufacture of synthetic resins and their conversion products with a knowledge of international trends in the plastics industry and marketing evaluation.

Background Information

As Job Description TRI-081-SFB (SF/ID).

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and Marketing of Acrylic Sheet in Developing Countries" United Nations, E.71.11.
B.21.
4. **Third Year Plan 1969-1973, Government of Trinidad & Tobago. Pages 251-254.**
5. **"The Market for Cashew Nut Kernels and Cashew Nut Shell Liquid" A. Date,**
Tropical Products Institute, Ministry of Overseas Development, London,
April 1965.

APPENDIX I

CONSTITUTION OF RELEVANT S.I.T.C. CODES

599-01 Synthetic Plastic Materials in Blocks, Sheets, Rods, Tubes, Powder and other Primary Forms

This heading includes synthetic plastic materials, in clots, film, flakes, foil, granules, dispersions, emulsions, lumps, plates, paste, profile shapes, solution, sticks and strips as well as in cellular, laminated and liquid form. Cloth or paper impregnated with synthetic plastic materials and having the characteristics of plastics are included in this heading. It excludes:

1. Cold moulding compounds prepared from bituminous substances with mineral or other fillers.
2. Reconstituted wood composed of wood shavings or other wood waste agglomerated with artificial resins or other organic binding substances.
3. Liquid polycondensation products which are not hardenable by heat.
4. Synthetic rubber.
5. Extruded artificial fibres, horsehair or straw.

oo0oo

Acrylics, Plastic
Alkyds
Aminoplasts
Aniline-formaldehyde
anilinoplasts

Bakelite, in primary forms

Casein, hardened
Celloidin
Cellophane
Celluloid
Cellulose acetate
Cellulose, Aceto-butyrato
Cellulose, Acetyl
Cellulose, benzyl
Cellulose, carboxymethyl
Cellulose derivatives
Cellulose, di-acetate
Cellulose esters, inorganic
Cellulose esters, organic
Cellulose ethers
Cellulose, formyl

Cellulose, methyl
Cellulose, nitrate, except collodion
Cellulose, nitro, except collodion
Cellulose, oxyethyl
Cellulose, propionate
Cellulose, regenerated, excluding vulcanized fibre
• Cellulose, tri-acetate
Cellulose varnish bases, dry or pasty extracts
Cellulose xanthogenate of
• Chloride, polyvinyl

Esters, cellulose, inorganic
Esters, cellulose, organic
Esters, polyallyl
Ethers, polyallyl
Ethyl-cellulose

Galalith
Gelatine, chemically hardened
Gun cotton

Melamine-formaldehyde

Novolaks
Nylon, in primary, unextruded forms

Paste, moulding of plastic materials
Perspex
phenolics
Phenoplasts
Photographic film unsensitized, unperforated
Plastic materials, synthetic, in blocks, sheets, rods, tubes, powder and other primary forms.
Plastic sausage casings, not seamed
Plastic starch
Plastic, transparent, for windows
Plastics, artificial, in primary forms
Plastics, artificial, scrap of
Plastics, artificial, waste of
Plastics, lignin
Plastics, proteinic
• Plastics, synthetic, in primary forms
Polyacrylic derivatives
Polyamides
• Polycondensation products, linear
Polycondensation products, plastic excluding liquid products which cannot be hardened by heat.
Polyethylene derivatives
Polyethylenes
Polyisobutylene
Polymerization products, artificial resins or plastics, excluding-liquid polymers which do not harden by heat, synthetic rubber.

Appendix I, Cont'd

Polymethanes
Polystyrene
Polythene
Polyurethanes
Polyvinyl derivatives
Polyvinylidene derivatives
Protein derivatives, hardened

Resins, alkyd
Resins, artificial, in primary forms
Resins, artificial, incorporating natural resins, in primary forms
Resins, coumarone-indene
Resins, melamine
Resins, phenolic
Resins, silicon
Resins, Silicone
Resins, urea
Resites
Resitols
Resols

Silicone fluids
Silicones, excluding elastics
Starch, chemically hardened
Super polyamides

Thiourea-formaldehyde

Urea-formaldehyde

Viscose, not threads or fibres.

533-03 Prepared Paints, Enamels, Lacquers, Varnishes, Artists colours, Siccatives
Paint Driers - and mastics

This heading consists of:

1. Colours prepared for final use
2. Paint driers, prepared
3. Dyes, prepared other than tolled preparations
4. Enamels
5. Glasses, ceramic

6. Lacquers
7. Lustrous liquid
8. Certain mastics
9. Paints prepared
10. Pearl essence
11. Pigments prepared for final use
12. Varnishes other than cosmetic varnishes.

o o o o o

Cement, resin

Colouring matters, put up in packings for retail sale for use as dyes

Colours, amusements, including colours boxed with accessories

Colours, ceramic, vitrifiable compounds

Colours, gouache

Colours, high-temperature

Colours made up for retail sale

Colours, prepared for final use, excluding printers

Colours, prepared, for use in the ceramic, enamelling or glass industries

Colours, students, including boxed with accessories

Colours, sub-enamel

Colours, super-enamel

Colours, vitrifiable

Colours, water

Driers, varnish, prepared for final use

Driers, paint, prepared for final use

Dyes, household, other than toilet preparations

Dyes, prepared, other than toilet preparations

Enamels

Enamels, ceramic

Filling materials for painters use

Glazes, ceramic

Japans

Appendix I, Cont'd

Lacquers

Lacquers, cellulose
Lustres, liquid
Lustres, liquid, aluminium
Lustres, liquid, chromium
Lustres, liquid, gold
Lustres, liquid, silver

Mastic, cellulose

Mastics, resin, cement

Opacifiers for use in the ceramic, enamelling or glass industries

Paints, anti-fouling

Paints, anti-peeling

Paints, asphalt

Paints, bituminous

Paints, caseine

Paints cellulose

Paints, enamel

Paints, luminous

Paints, oil

Paints, prepared

Paints, varnish

Paints, rubber base

Paints, water

Paints, weather-proof

Pearl essence

Pigments for use in the ceramic, enamelling or glass industries

Plastic, marbel workers

Powder, iron, prepared as colours

Powder, prepared as colours

Primers, prepared

Putty

Putty, glaziers

Shellacs, prepared

siccatives

Slips used to coat ceramic ware

Stopping materials for painters use

Varnishes, cellulose

Varnishes, oil

Varnishes, other than cosmetic varnishes

Varnishes, spirit

Wood, plastic

Appendix I, Cont'd

641-07 Paper and Paperboard, Coated, Impregnated, Vulcanized, Etc., Other than Bituminized or Asphalted

Paper, paperboard and laminated paper impregnated with synthetic plastic materials but retaining the characteristics of paper or paperboard are included in this item.

o o o o o

Board, building of pulp, bonded or impregnated

Board, building, of wood pulp, bonded or impregnated

Paper, adhesive

Paper, art, coated

Paper, carbon- in bulk, rolls or sheets

Paper, chrome

Paper, coated and varnished

Paper, coated, other than bituminized or asphalted in rolls or large sheets

Paper, coated with albumen

Paper, coated with barium sulphate

Paper, coated with chalk

Paper, coated with dextrin

Paper, coated with gelatine

Paper, coated with glue

Paper, coated with granulated cork

Paper, coated with gypsum

Paper, coated with metal powder

Paper, coated with pigments

Paper coated with sawdust

Paper, coated with shellac

Paper, coated with starch

Paper, coated with synthetic resins, e.g., nitrogellulose

Paper, coated with textile dust

Paper, coated with waxes

Paper, coated with zinc oxide

Paper, design-printed

Paper, enamelled

Paper, externally reinforced with textile or wire

Paper, flock, i.e., coated with textile dust

Paper, for wrapping and writing, printed with colours, designs, motifs, stripes

Paper, for wrapping and writing printed with names of traders, products

Paper, gilt

Paper, graphite, other than imitation slate

Paper, grease proof

Paper, gummed

Paper, impregnated, excluding bituminized or asphalted

Paper, impregnated, translucent or transparent

Paper, impregnated with artificial resin

Paper, impregnated with chemicals

Appendix I, Cont'd

Paper, impregnated with insecticides, e.g., D.D.T.
Paper, impregnated with oil
Paper, impregnated with waxes
Paper, indicator, e.g., rubberized paper
Paper, jaspe
Paper, litmus
Paper, manifold, oiled
Paper, manifold, waxed
Paper, mica-coated
Paper, mineral coated, art printing
Paper, paraffin-coated
Paper, pole-finding
Paper, porcelain
Paper, printing, high grade, coated in bulk
Paper, printing, high grade, design printed in bulk
Paper, printing high grade, surface-coloured, in bulk
Paper, rubberized
Paper, salicylated
Paper, silvered
Paper, stearin-coated
Paper, stencil, in rolls or large sheets
Paper, marbled
Paper, tracing, in rolls or large sheets
Paper, unsensitized photographic base
Paper, varnished
Paper, velveted
Paper, vulcanized
Paper, wallpaper base, impregnated
Paper, waterproof, not asphalted or bituminized
Paper, wrapping, oiled
Paper, writing, high grade, coated, in bulk
Paper, writing, high grade, design, printed, in bulk
Paper, writing, high grade, surface-coloured in bulk
Paperboard, coated and varnished
Paperboard coated, other than bituminized or asphalted
Paperboard, coated with albumen
Paperboard, coated with barium sulphate
Paperboard, coated with chalk
Paperboard, coated with dextrin
Paperboard, coated with gelatine
Paperboard, coated with glue
Paperboard, coated with granulated cork
Paperboard, coated with gypsum
Paperboard, coated with pigments
Paperboard, coated with sawdust
Paperboard, coated with shellac
Paperboard, coated with starch
Paperboard, coated with synthetic varnishes, e.g., nitrocellulose
Paperboard, coated with textile dust

Appendix I, Continued

Paperboard, coated with waxes
Paperboard, coated with zinc oxide
Paperboard, grease proof
Paperboard, impregnated, other than bituminized or asphalted
• Paperboard, impregnated with artificial resin
Paperboard, impregnated with certain chemicals other than tar and bitumen
Paperboard, impregnated with insecticides e. g., D. D. T.
• Paperboard, impregnated with oil
Paperboard, impregnated with waxes
Paperboard, impregnated, insulating
Paperboard, varnished
Paperboard, vulcanized
Paperboard, vulcanized, in rods and tubes
Paperboard, waterproof
Pulp fibre, vulcanized

APPENDIX II

LIST OF MANUFACTURING ORGANIZATIONS VISITED

<u>Visit No.</u>	<u>Firm</u>	<u>Aspect</u>	<u>Affiliation</u>
1.	Styrotex Ltd.	Thermoplastics moulding	Subsidiary of Alstons Ltd.
2.	Sissons (West Indies) Ltd.	Resin User (Alkyds etc) Paints.	Sissons Ltd. (U.K).
3.	Spra-Glass Division, Trinidad Steam Laundry	Thermoplastics moulding and resin user (GRP)	-
4.	Plastic Foams Ltd.	Resin user (PU Foam)	-
5.	Glastron Boats Ltd.	Resin user (GRP)	Under license to Glastron, U.S.A.
6.	Handy Equipment Ltd.	Resin user (Adhesives)	Under license to Borden Co. (U.K)
7.	Berger Paints Ltd.	Resin user (paints)	Associate Company of Lewis Berger Ltd. (UK)
8.	Coates Bros. (Caribbean) Ltd.	Resin user (printing inks)	Subsidiary of Coates Bros. (UK)
9.	Century Eslon Ltd.	Thermoplastics extrusion and moulding	Associated with Seikisui (Japan) Marketing restricted to CARIFTA.
10.	E. Viera Ltd.	Import agents	Polymer Caribbean
11.	Dunlop Ltd.	Resin user (Adhesives and rubbers) Automotive re- placement trends	The Dunlop Co. (UK)
12.	Auto Chemicals Ltd.	Resin user (Adhesives)	-
13.	Hi Grade Products Ltd.	Thermoplastics moulder	-
14.	Polymer Caribbean Ltd.	Thermoplastics conversion	Member of Polymer International Group
15.	I.C.I. Paints (West Indies) Ltd.	Resin user (Paints)	Subsidiary-Imperial Chemical Industries Ltd. (UK)

Visit No.	Firm	Aspect	Affiliation
16.	Narine Persad	Resin user (PU foams) and furniture manufacture	-
17.	Fibreglass Manufacturing Trinidad Ltd.	Resin user (GRP)	-
18	Consolidated Appliances Ltd.	Thermoplastics sheet converter	Part of a Jamaican group.
19.	Texaco Ltd.	Raw Materials - plans	Texaco International
20.	Advanced Plastics Ltd.	Thermoplastics sheet conversion & mouldings.	-
21.	Amalgamated Industries Ltd.	Automotive Assembly	-
22.	L. J. Williams	Resin user (adhesives)	Under license to Evode Ltd. (UK)
23.	East End Foundry	Potential resin user	Subsidiary of Alstons Ltd. Agent for Fosco Ltd., UK.
24.	Doneon Ltd.	Thermoplastics sheet converter	-
25.	Metal Box Co. (Trinidad) Ltd.	Packaging	Subsidiary of Metal Box Co. Ltd., UK.
26.	Trinidad Footwear Ltd.,	Thermoplastics moulder	Part of Bata Group
27.	Prof. Richards (U.W.I.)	Bagasse Board Project	-
28.	Abmit Ltd.	Battery manufacture	Subsidiary of Chloride Group, UK.
29.	Acme Motor Supplies Ltd.	Resin user (body fillers)	-
30.	Ibis Trading Co.	Decorative laminates	Imports - "Laminate" Canada
31.	Lim Plastics	Thermoplastics converter	-
32.	Myerson Mouldings Ltd.	Thermoplastics converter (teeth)	Subsidiary of Myerson Tooth Co., U.S.A.
33.	Thomas Peake & Co. Ltd.	Decorative Laminates.	Import "Arborite."

<u>Visit No.</u>	<u>Firm</u>	<u>Aspect</u>	<u>Affiliation</u>
34.	Federation Chemicals Ltd.	Raw-materials (Urea)	-
35.	Lever Bros. Ltd.	Raw-materials (glycerol) and packaging	Subsidiary of Unilever Ltd. UK.
36.	Trinidad Rope Works Ltd.	Thermoplastics fibre converter	Subsidiary of Hawkins & Tipson (Marlow Ropes) Ltd., UK
37.	Angelo Plastics	Thermoplastics sheet fabricator.	-
38.	Eastern Industries Ltd.	Thermoplastics moulder	-
39.	Electrical Industries Ltd.	Thermoplastics extruder (cables)	Subsidiary of Neal & Massey - formerly owned by A.E.I. Group UK, who still collaborate by testing.
40.	Dr. K. Bahadoorsingh	Entrepreneur (Thermoplastics interests)	-
41.	International Recording Co. Ltd.	Thermoplastics converter (Records) and packaging	"
42.	Sherwin Williams Ltd.	Import agents (paints and body fillers)	Sherwin Williams Ltd. U.S.A.
43.	Caribbean Engineering Ltd.	Thermoplastics sheet converter	Subsidiary of Thorn Electric, U.K.
44.	Flexipak Ltd.	Thermoplastics film converters (packaging)	Owned by National Packaging Ltd. Jamaica.
45.	Super Pak Ltd.	Thermoplastics film converters (packaging)	-
46.	Natasha Co. Ltd.	Thermoplastics converters	-
47.	Roods & Co., Ltd.,	Entrepreneur (polymerization process)	-
48.	Hoechst	Thermoplastics raw materials	Farbwerke Hoechst A. G.

<u>Visit No.</u>	<u>Firm</u>	<u>Aspect</u>	<u>Affiliation</u>
49.	Shell Trinidad Ltd.	Thermosetting raw materials	Shell International Holland & UK.
50.	Rooks Oilfields & Engineering Supplies Ltd.	Assignee of crude oil patent (Applied for)	-

TELEPHONE INTERVIEWS

Gordon Grant & Co. Ltd.	Decorative laminates	(Formica)
Paper & Plastic Converters Ltd.	Thermoplastics extrusion	-
Geddes Grant & Co., Ltd.,	Thermoplastics sheet.	I.C.I. Ltd., U.K.

PROGRAMME

9.00 to 9.25 a.m.	Registration of delegates	
9.30 a.m.	Address of Welcome	Prof. I. E. S. Braithwaite, Pro-Vice-Chancellor, UWI; Member of Board of Management, CAREPI.
9.40 a.m.	Inauguration	The Hon. George Chambers, Minister of Finance, Planning and Development.

MORNING SESSION

Chairman - Mr. Hollis Charles, Co-Director, CARIRI

9.55 a.m.	"Flow Properties of Thermoplastics"	Dr. P. N. Bruce, Dept. of Chem. Eng., UWI.
10.20 a.m.	Discussion	
10.30 a.m.	"Extrusion of Thermoplastics with Special Reference to Rigid PVC"	Mr. Leon Wharwood, Century Eslon Ltd.
10.55 a.m.	Discussion	
11.05 a.m.	COFFEE	
11.20 a.m.	"Film Extrusion"	Mr. N. Lai Fook, Polymer Caribbean Ltd.
11.45 a.m.	Discussion	
11.55 a.m.	"Injection Moulding"	Mr. E. Norfolk, Polymer Caribbean Ltd.
12.20 a.m.	Discussion	
12.30 a.m.	LUNCH	

AFTERNOON SESSION

Chairman - Mr. Fenrick de Four, President, Association of Professional Engineers.

1.30 p.m.	"Epoxide Resins"	Mr. Gerrard Dennis, Shell Trinidad Ltd.
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Programme Cont'd

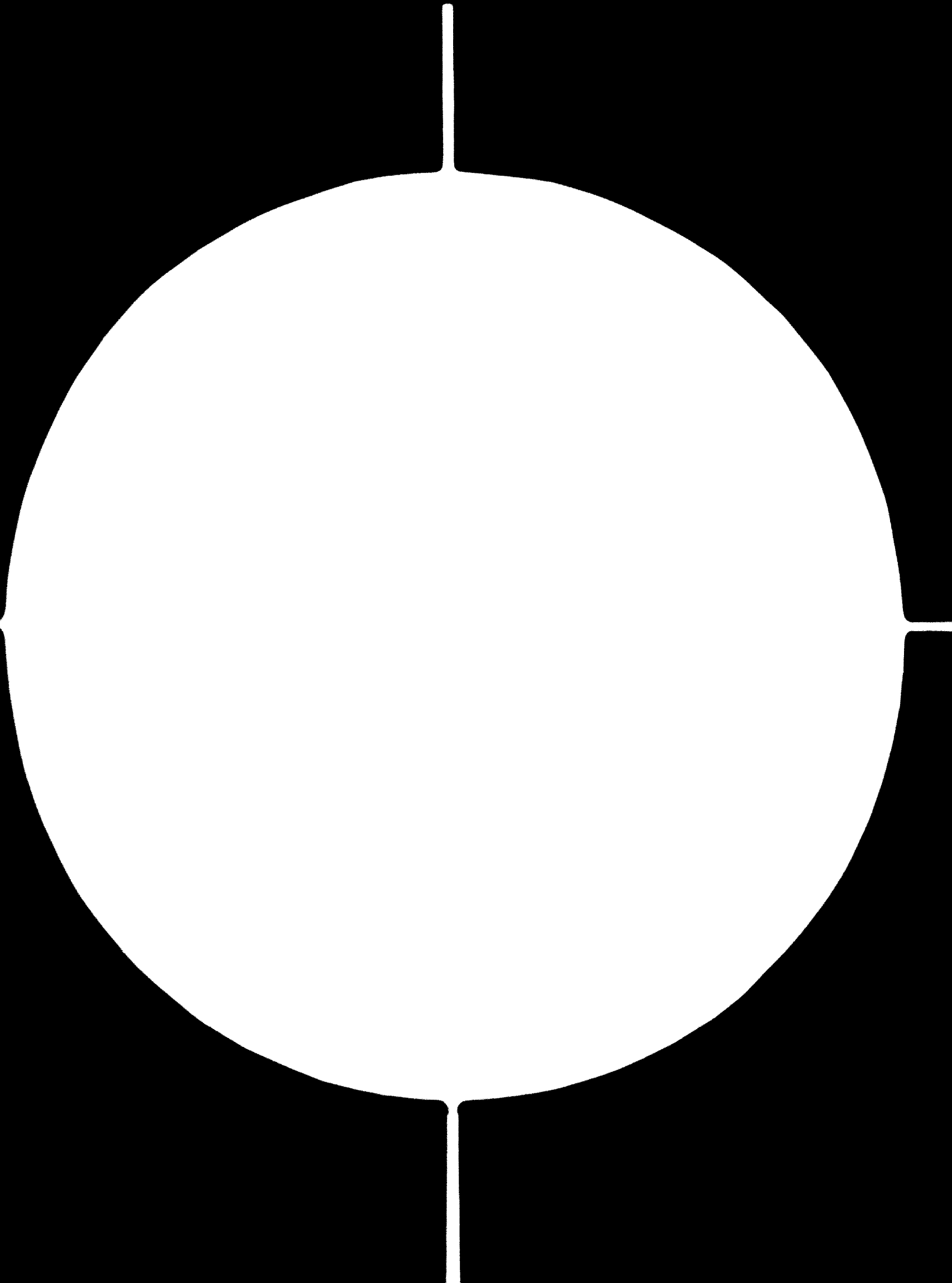
1.55 p. m.	Discussion	
2.05 p. m.	"Reinforced Plastics"	Mr. J. E. S. Whitney, UN Consultant, CARIKI
2.30 p. m.	Discussion	
2.40 p. m.	TEA	
3.00 p. m.	Discussion Panel:	Dr. P. Bruce, Messrs. F. Nordstrom, F. Thompson, J. Whitney & M. Williams
4.00 p. m.	Closing Remarks	Mr. Hollis Charles, Co-Director, CARIRI

Organizing Committee: J. E. S. Whitney (Convenor)
Dr. P. Bruce
Mr. Hollis Charles
Mr. Eiliv Sodahl

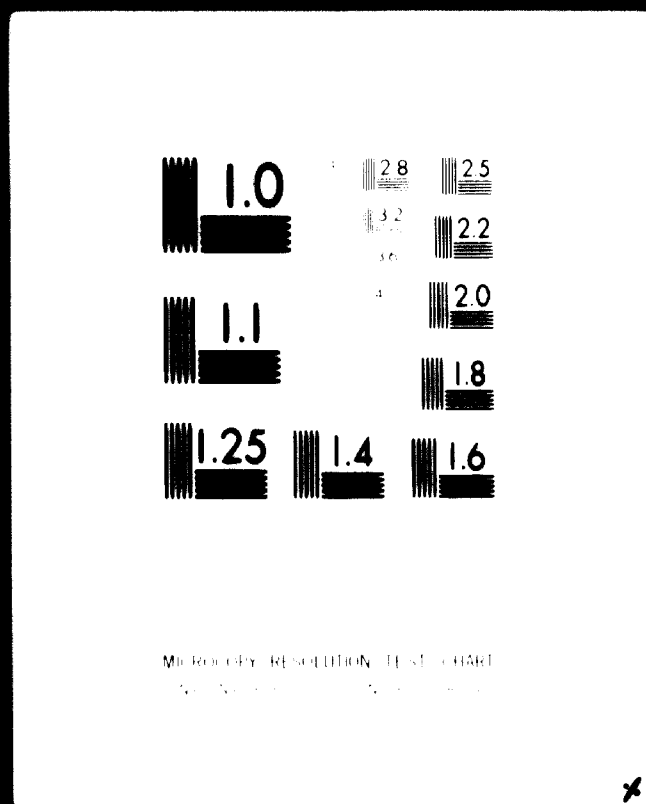
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CARIPI - UNI - APETT

Symposium on plastics technology:

14 July 1972

UNI, St. Augustine.

Paper No. 6 - REINFORCED PLASTICS - J.E.S. Whitney

REINFORCED PLASTICS

Although the general definition of Reinforced Plastics encompasses substantially all systems of plastic binders in combination with fibrous reinforcing fillers, which may range from cellulosic to carbon, it is proposed to concentrate our attention upon the Glass Reinforced Plastic materials, GRP, which are derived mainly from combinations of unsaturated polyester resins with a variety of glass fibre reinforcements.

Having outlined the unsaturated polyester resin systems in my Seminar Papers (Pages 23 to 25) I now propose to consider their use and behaviour in the manufacture of reinforced composites in the light of end-use applications and types of reinforcement employed.

Resin Cure

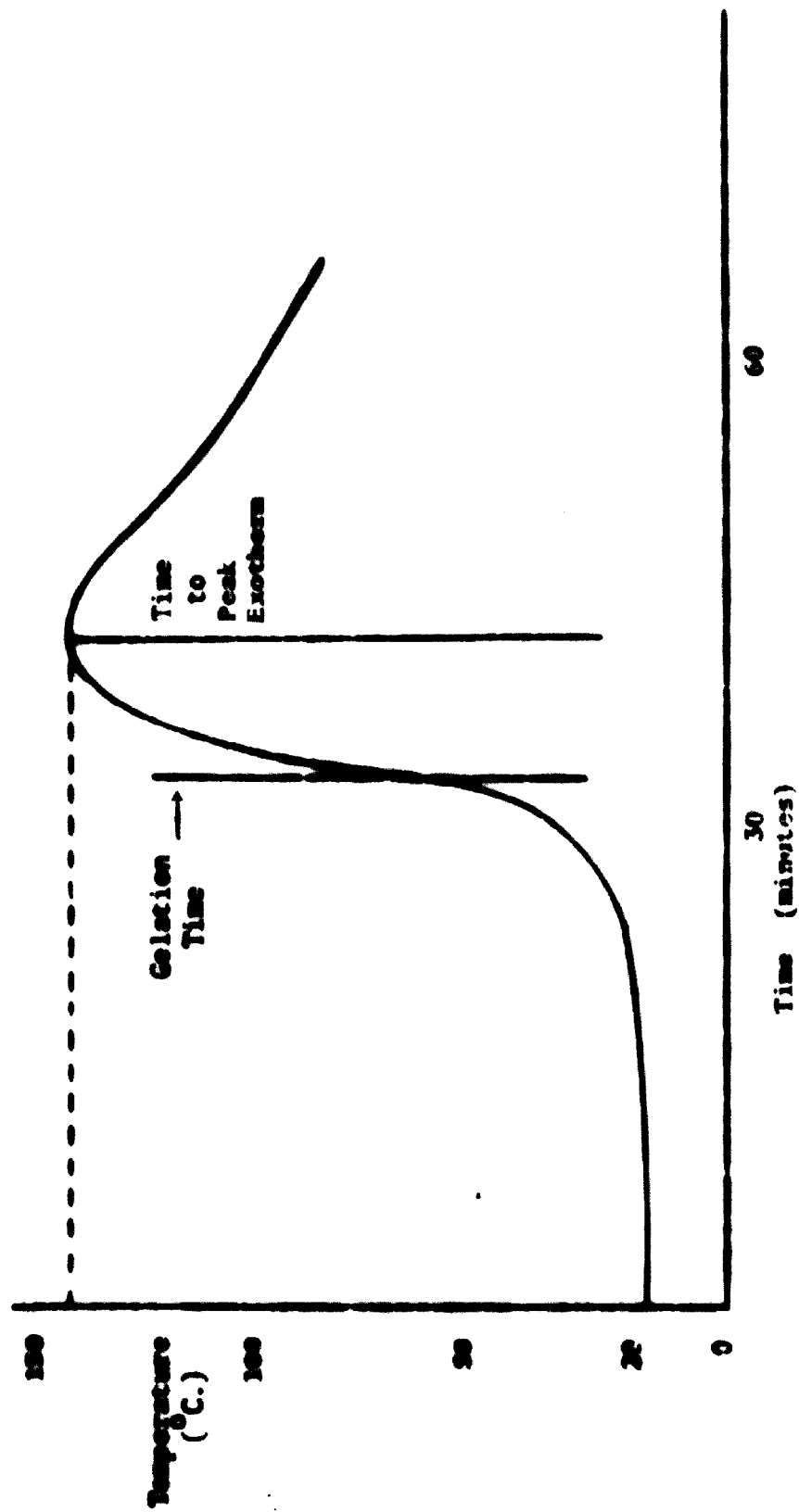
Unsaturated polyester resins polymerize by means of a free-radicle mechanism in the presence of peroxide catalysts (see Seminar Paper pages 8 to 9). This reaction being characterised by the production of exothermic heat throughout its course. Diagram 1 indicates a typical temperature-time pattern obtained by inserting a thermocouple into a volume of resin after the introduction of catalyst and promoter. It will be noted that the onset of gelation occurs quite early during the propagation stage and that the temperature continues to rise sharply after gelation, sometimes to above the boiling point of the styrene monomer. This phenomenon can lead to severe internal stressing and crazing in both castings and resin-rich areas which may be introduced by the faulty lay-up of composites. Because of their curing mechanism unsaturated polyesters are inevitable air inhibited thus exposed surfaces require the use of barriers, such as cellophane, during cure.

The rate of gelation and cure is dependent upon a number of factors and may be controlled by attention to the following major contributions:

- i. Bulk of resin and surface to volume ratio.
- ii. Inhibitor content and maleic anhydride content of the resin.
- iii. Type and proportions of catalyst and promoter used.

Diagram I

Dypical Exotherm of Catalyzed/Promoted Resin



Catalyst - Promoter Systems

Catalysts

For many years the catalysts employed for curing unsaturated polyesters were selected from a range of peroxides and hydroperoxides. More recently azo initiators, such as 2,2'-azobisisobutyronitrile, have been introduced but they have not yet significantly encroached on peroxides. Selection of a suitable catalyst for any particular application is dependent upon its precise stability and form. Catalysts are invariably characterised by the temperature range over which decomposition occurs, as indicated in Table 1 below.

TABLE I

Stability of Typical Peroxide Catalysts. (Approximate)

<u>Type</u>	<u>Half-Life (Minutes)</u>		
	<u>85°C</u>	<u>100°C.</u>	<u>130°C.</u>
Benzoyl peroxide (Pasted in dibutyl phthalate)	132	25	1.3
Lauroyl peroxide (Granular solid)	30	5	-
Methylethylketone Peroxide (Solution)	Short		
t-butyl peroxybenzoate (Liquid)	5 days	18 hours	35

Promoters

While when effecting cure at elevated temperatures the peroxide catalyst decomposes spontaneously, thereby initiating cure. In order to initiate cure at ambient temperatures substances capable of inducing decomposition of the peroxide rapidly must be introduced. The most widely used of these include organo salts of polyvalent metals; such as cobalt and vanadium, tertiary amines, such as N.N. dimethyl aniline and mercaptans, such as lauryl mercaptan.

Combinations

While during the early days of reinforced plastics benzoyl peroxide in the absence of a promoter was used for effecting cure at elevated temperatures and in the presence of amine promoters for ambient temperature cure, with respect to the latter process, it has now lost its popularity in favour of the metal salt promoted M.E.K. peroxide and cyclohexanone hydroperoxide catalysts, which result in products of superior colour. In general catalyst-promoter proportions are maintained at minimal levels, pro rata to the required curing schedules. Normally, the amount of catalyst exceeds 1% with the promoter concentration being maintained at as little above 0.5% as possible. As an indication the influence of catalyst - promoter proportions upon gelation times at various concentrations is illustrated in Tables II and III below.

TABLE II
Effect of Variation in Promoter Concentration

Catalyst	M.E.K. Peroxide (MEKP)				Cyclohexanone Hydroperoxide (CHP)			
Resin (p.b.w.)	100	100	100	100	100	100	100	100
Catalyst -do-	2	2	2	2	2	2	2	2
Promoter -do-	1	2	3	4	1	2	3	4
Gel time at 20°C. (minutes)	65	17	12	10	105	44	30	23

TABLE III

Catalyst	M.E.K. Peroxide			Cyclohexanone Hydroperoxide		
Resin (p.b.w.)	100	100	100	100	100	100
Catalyst -do-	1	2	3	2	3	4
Promoter -do-	2	2	2	2	2	2
Gel time at 20°C. (minutes)	90	40	20	25	17	9

It should be noted that a direct comparison between Tables II and III cannot be made as in Table II; the promoter was added in the form of a 1% cobalt metal siccato solution in phthalate plasticiser, and in Table III as a 1% cobalt metal octoate solution in monomeric styrene.

In view of the sensitivity of the peroxide catalysts both towards heat and in some cases towards shock and friction, they are normally marketed in the form of pastes or solutions in water or phthalate plasticisers, in the former instance care should be taken to avoid drying out of the paste, particularly between friction promoting surfaces such as glass stoppered bottles.

Cobalt based promoters in the form of naphthenate, octoate or siccato are normally available as solutions, containing 1% metal, in diamethyl phthalate or monomeric styrene. More recently vanadium based promoters have become available. While being considerably more expensive than those based on cobalt they offer advantages in terms of efficiency, i.e. economy in use, faster gelation and hence paler coloured products.

Resin Properties

The effect of major variants in unsaturated polyester resin formulations are briefly described in my Seminar Paper (page 24). I do not propose to enlarge on this aspect now, but outline the properties of selected resins in the cured and uncured states. For this purpose I have chosen three typical commercial resins.

- Resin No. 1 - A general purpose polyester based upon propylene glycol maleate/phthalate.
- Resin No. 2 - A chemical resistant, high heat distortion grade of isophthalic polyester.
- Resin No. 3 - An antimony oxide filled, phosphate ester plasticised, self-extinguishing resin for structures conforming to fire-retardant specifications.

TABLE IV

Uncured Resin Specifications

Resin No.	Units	1.	2.	3.
Appearance		Transparent	Transparent	Opaque
Viscosity at 25°C.	cs.	400 - 650	750 - 1,200	400 - 600
Volatile Content	%	36 - 40	39 - 43	34 - 38
Acid Value	mgms. KOH/gm.	21 - 29	18 - 26	-
Gelation Time * at 25°C.	mins.	7.5 - 10.5	8.5 - 11.5	8 - 11

* Gelation time of 15 gm. sample containing 2 p.p.h. of an MEKP catalyst and 3 p.p.h. of a cobalt octoate promoter.

TABLE V

'As Cast' Properties (Unfilled)

Property	Unit	Resin No. 1	Resin No. 2	Resin No. 3
Tensile strength	p.s.i.	6,000	6,700	5,750
Young's modulus in Tension	p.s.i.	5.5×10^5	5.7×10^5	5.7×10^5
Flexural strength	p.s.i.	15,500	15,000	8,700
Modulus in Flexure	p.s.i.	5.5×10^5	5.3×10^5	5.4×10^5
Impact Strength (Izod)	ft. lbs/inch of notch	0.25	0.28	0.12
Brinell Hardness (5mm ball 125 kg wgt.)	No.	35	30	27
Heat Distortion Temp. *	°C.	69-73	115	70-74
Water Absorption at 23°C for 24 hrs.	mg.	16	24	18
Leaching at 23°C for 24 hrs.	mg.	Nil	Nil	0.5
Flexural Strength after 2 hr. boil	p.s.i.	12,100	12,000	7,340
Electrical Properties				
Power Factor (1,000 cycles at 23°C.		0.001	0.0025	0.001
Permittivity - do		3.22	3.00	3.15
Volume Resistivity	ohms/cm	1.34×10^{15}	1.25×10^{15}	1.25×10^{15}
Breakdown Voltage	volts	350	340	400

Note - With the exception of *, which was tested according to A.S.T.M. D648-56, all tests were carried out according to B.S.S. 2792.

Reinforcement

In order to maximise strength and uniformity of composites the following factors predominate:

1. The completeness of wetting of individual glass fibres.
2. Adhesion between cured resin and glass.
3. Continuity of reinforcing fibres, which may in certain cases be directional.
4. Absence of voids.
5. Avoidance of resin-rich areas and maximisation of the reinforcement to resin ratio.

Item 1 - involves such considerations as resin flow in the uncured state and elimination of deleterious binders and dressings involved in the reinforcement manufacture, in particular starch based sizes.

Item 2 - The ultimate extent to which the glass-resin bond is maximised is exemplified by the use of reinforcing glass fabrics in which the fibres have been chemically treated in order to obtain primary bonding. An example of this is provided by volanising or treatment for example with methacrylato-chromyl chloride. In which the chromyl chloride reacts with hydroxyl groups on the glass fibre surface and the methacrylato group co-polymerizes into the resin phase.

Item 3 - Can be demonstrated in many service applications involving the use of glass fabrics and in the manufacture of pipes and tanks from continuous glass fibre rovings.

Item 4 and 5 are inter-related as they are controlled by mechanical factors during lay-up, in particular the removal of bubbles from and between each ply and the use of sufficient pressure to express surplus resin.

Reinforcing Materials

The two basic types of glass employed in the manufacture of reinforcing materials are "A" Glass, a conventional soda glass of high alkalinity, and "E" Glass a low alkali boro-silicate glass. "E" Glass is superior to "A" Glass, particularly in respect to transparency in the finished moulding,

strength and resistance to weathering and acids.

Mainly from price considerations the use of woven fabrics as major reinforcements has declined in favour of bonded fibre mats and the like. Nevertheless, even in quite common place items it may be desirable to employ localised areas of fabric where stresses may be encountered during use. The main general purpose reinforcements in common use include:

1. Chopped Strand Mat.

Consists of strands of glass fibre threads, approximately two inches long, laid down in random pattern and held by a suitable binder, usually polyvinyl acetate. It is the most generally used reinforcement for hand lay-up techniques, particularly for large objects. It is available in both "A" Glass and "E" Glass in substance weights ranging from 1 oz to 2½ oz per square foot.

2. Needled Mat.

Consists of strands, approximately two inches long, randomly laid and held on to a glass tissue by mechanically needling with glass threads. It is only manufactured in "E" Glass and is available in weights ranging from 1 oz to 4 oz. Although having the advantage of freedom from binder it is more springy and open than chopped strand mat and its use is confined to applications where high resin contents are acceptable.

3. Roving and Chopped Rovings.

Rovings consist of untwisted multi-strand continuous filaments. They are supplied in the form of coils known as cheeses, in weights ranging from 3 to 33 lbs, in which the number of unwinding ends may be varied to suit the application. Apart from the use of rovings in items produced by winding, continuously chopped rovings are being increasingly employed in spray lay-up techniques and in pre-forms for matched metal mouldings.

4. **Surface Tissue.**

Consists of a thin fibrous veil of lightly bonded staple glass fibres. It is employed in hand lay-up and spray-up techniques to provide a resin-rich surface and as a barrier between the coarser mat fibres and surface gel coats. In this manner it improves weathering resistance by preventing wicking.

5. **Reinforcement Cord.**

Cords of 1/8 and 1/4 inch nominal diameter can be used for edge strengthening and provision of reinforcing ribs.

Moulding Techniques

Techniques employed in the fabrication of GRP items may be conveniently subdivided into hand-lay up methods and mechanical methods.

Contact moulding by hand lay-up is the best known technique for producing the widest range of items. It is normally effected in female moulds which can be constructed from simple, cheap materials including plaster, wood, cast resin (phenolic or epoxy), or glass reinforced polyester itself, or easily formed metal sheet, particularly aluminium. A convenient procedure for prototype or 'one-off' tailored production items is to prepare a plaster cast from either a wooden pattern or an item to be reproduced.

Essential requirements in mould preparation are:

- i. With porous mould materials, particularly plaster and wood, it is necessary to apply an efficient sealing medium, the commonest of which include shellac and synthetic resin lacquers of the cold-curing variety.
- ii. A release agent must be applied to the mould surface before laying up. This could include a variety of waxes applied from solution or paste form, aqueous polyvinyl-alcohol solutions or, in the case of flat or corrugated sheets, uncoated cellophane film.

Outline of Hand Lay-Up Method:

A uniform layer of a catalysed thixotropic resin which may, if required, be pigmented, is applied uniformly to the mould interior at a spread of less than 400 gm/sq.m. Immediately after the onset of gelation of this coat the main reinforcement is applied and catalysed resin poured over and worked in by suitable roller to insure even distribution and removal of bubbles. The thickness of the moulding being determined by the number of layers and weight of the mat employed. A layer of uncoated cellophane is then applied over the entire interior surface of the moulding to eliminate contact with air. Resin cure then proceeds at a rate determined by catalyst/promoter concentrations and whether or not supplementary heating is employed. When adequate cure has been achieved and the moulding has sufficiently cooled, it is extracted from the mould and subjected to post-curing storage.

Spray-Up Process:

Is substantially similar to the hand lay-up process except that in place of separate application of mat and catalysed resin chopped rovings are applied to the surface of the gel coat by means of an air spray-cutter. Simultaneously catalysed resin is spray applied. When an adequate layer of resin/glass has been applied consolidation and removal of air bubbles is effected by rolling. Where thick layers are required it is preferable to effect a gradual build-up, consolidating and removing air between each layer of sprayed ingredients.

Strength characteristics between the two techniques are not dissimilar but the spray-up process offers significant advantages with regard to labour costs, scrap reduction and uniformity. Either techniques may be employed in the manufacture of items over a very wide range of sizes. With certain size limitations rubber bag techniques; in which either positive pressure or vacuum is utilised; can be employed to improve consolidation, minimise resin consumption and facilitate a reasonable degree of heat cure.

Matched Metal Moulding:

In this process chopped rovings are sprayed on to a pre-shaped wire mesh former and lightly bound with polyvinyl acetate emulsion. The preform is located in a female metal mould (steel or aluminium) catalysed resin is introduced and the male tool applied at a pressure in the order of 100 p.s.i. cure being effected rapidly at temperatures in the order of 120°C. This process is largely confined to the production of small items such as safety helmets.

TABLE VI

Properties of Mould Construction Materials

MATERIAL	APPROXIMATE PRODUCTION LIFE	FEATURES
Plaster	Maximum 10 off if adequately hardened, e.g. by incorporating a urea-formaldehyde resin.	Suitable for prototype and short runs only. Finish usually poor. Must be sealed.
Wood	Maximum 50 off.	Preparation depends on expensive machining. Must be sealed or varnished.
Fibre reinforced plastics.	300 to 1,000 off.	Most popular - can be based upon epoxy or polyester resins with glass or sisal reinforcement. Amenable to heat accelerated curing.
Sheet Metal	Over 1,000 off if distortion avoided.	Only suitable for simple shapes. Very suitable for heat curing.
Machined steel or aluminium.	Indefinite	Initial cost high, usually too heavy for large items, can be readily heated for fast curing. Amenable to pressure.

Properties of Glass Fibre Reinforced Polyesters

While the ultimate properties of reinforced plastics are dependent upon a variety of factors the most important include:

1. The volume ratio of fibre to resin: Physical properties reach an optimum when consolidation eliminates surplus resin. In hand lay-up techniques the maximum glass content achievable without encountering a risk from voids is in the order of 40% by weight. Pressures employed in matched die moulding increase this value to about 50%. Rubber bag techniques give intermediate values.
2. Reinforcement continuity and direction: Tensile strength and modulus in the direction of continuous reinforcement is naturally enhanced. Where required woven fabrics tapes and cords may be utilised for particular effects.
3. Resin Type: Except in special situations involving the use of more expensive epoxy resins or fibre treatments the various types of polyester resins do not differ greatly in their strength characteristics, unless they vary in their flexibility. Their principal differences are directed towards achieving particular properties such as chemical resistance, fire retardance, transparency and economics.

As sections of mouldings incorporating for example gel coat, surface tissue and chopped strand reinforcement are not uniform, precise strengths and other physical properties cannot be exactly forecast. A reasonable indication, however, is given by examination of the properties of flat laminates based upon "E" Glass chopped strand mat, general purpose resin and containing 35% by weight of glass.

TABLE VII

Properties of Flat GRP Laminates

(Average values attainable under laboratory conditions)

Property	Unit	Value
Density	lbs/in ³	0.54
Tensile Strength	p.s.i.	2×10^4
Flexural Strength	p.s.i.	2×10^4
Compressive Strength	p.s.i.	2×10^4
Young's Modulus:		
In Tension	p.s.i.	1.2×10^6
In Flexure	p.s.i.	1.3×10^6
Impact Strength- Izod.	ft. lbs/inch of notch	15
Thermal Conductivity	cal/sec/cm/ ^o C/cm ²	2.5×10^{-6}
Coefficient of Linear Expansion.	per ^o C.	16×10^{-6}

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CLASSIFICATION AND MAJOR APPLICATIONS
OF SYNTHETIC POLYMERS

INTRODUCTORY SEMINAR
Tuesday 13 April 1972

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Paper 1

FUNDAMENTAL ASPECTS OF CLASSIFICATION

"The noun *plastic* has been applied to embrace a wide range of polymeric materials which, in the finished state, are not and must not be plastic. At some stage, however, during the formation of an article from a synthetic polymeric material it goes through a *Plastic state*. *Plastic* is thus an adjective describing this state of having the capacity to flow under the influence of external forces. The use of the more correct term *Synthetic polymeric materials* is, therefore, preferred and will be used throughout the seminar, to avoid misunderstanding."

If one considers the variety of synthetic polymers in terms of such parameters as physical, chemical and mechanical properties, chemical composition, mode of synthesis it becomes obvious that their classification may be effected in a variety of ways. From the considerations imposed by time alone I do not intend to discuss this aspect but to demonstrate the most fundamental and generally accepted classification which is based upon molecular structure from which all their properties derive. In so doing it will be necessary to start from scratch and consider in basic terms the derivation and synthesis of polymeric materials.

Molecules can exist in the following forms:

- i. Discrete entities of precise structure, shape, composition and physical properties. This class is exemplified by all covalently bonded, mainly organic, chemical compounds.
- ii. Macromolecules which are linear in shape, based upon chains of carbon atoms or interdispersed carbon and other polyvalent atoms such as oxygen. This group is exemplified by the well-known class of *Thermoplastic*; or heat fusible; polymers. They are not precise entities as are those in Group i, but inevitably consist of mixtures of similar molecules of varying chain lengths and molecular weights.

- iii. Macromolecules having two-dimensional or planar shapes again of imprecise size and shape. This group is exemplified by such naturally occurring materials as graphite and mica.
- iv. Macromolecules of three-dimensional structure of quite indeterminate molecular weights. This group is exemplified by the end, or cured, products of the thermosets.

In particular respect of physical properties under the influence of heat materials in:

- Group i. Have precise melting points, boiling points etc. and generally dissolve to form newtonian solutions.
- Group ii. Soften and become fusible over a temperature range. Dissolve to form non-newtonian solutions, particularly at high concentrations.
- Group iii. Have not been synthesised, those occurring naturally being unaffected by heat up to their decomposition temperatures. Insoluble.
- Group iv. Also insoluble and infusible.

This main classification was first propounded by Kienle during the 1920's as a result of studies made on the reaction between dibasic acids, in particular phthalic acid and mono di and tri hydric alcohols, namely, ethanol ethylene glycol and glycerol. (See Diagram 1).

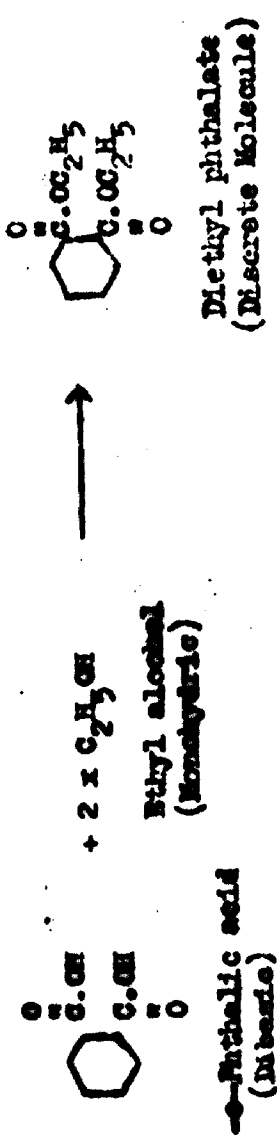
Hence Kienle postulated that:

- Reaction between two difunctional molecules gave rise to linear macromolecules.
- Reaction between a difunctional molecule and a tri functional molecule or one of higher functionality than three gave rise to a three-dimensional network structure (gel) eventually leading to an infusible, insoluble product.

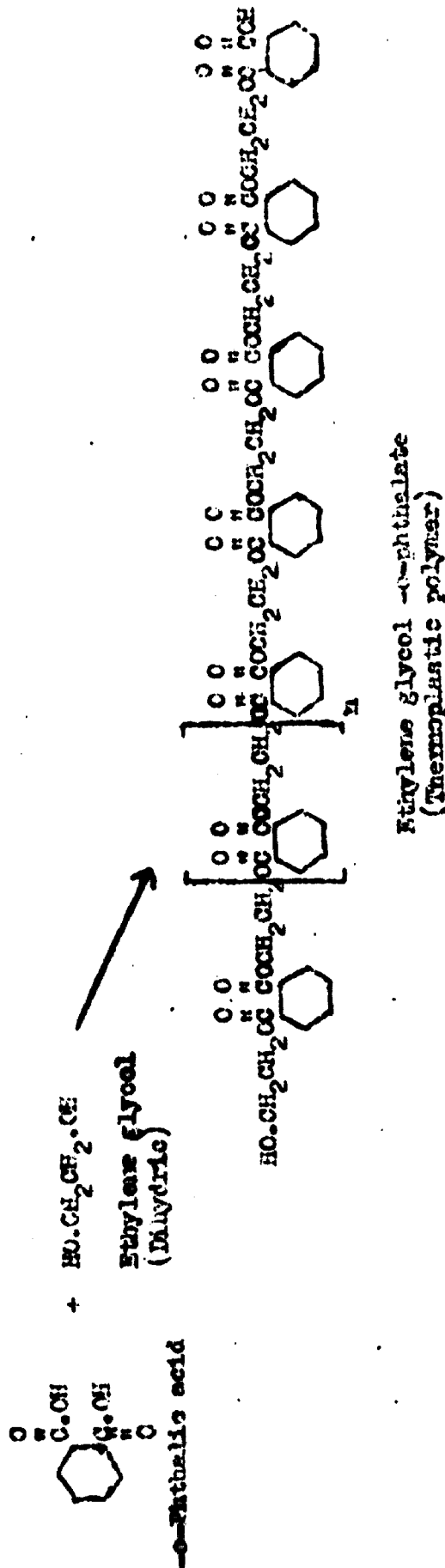
DIAGRAM 1.

KIEHL'S FUNCTIONALITY POSTULATES

Case 1. Monofunctional compounds react with Monofunctional compounds to form Discrete molecules.



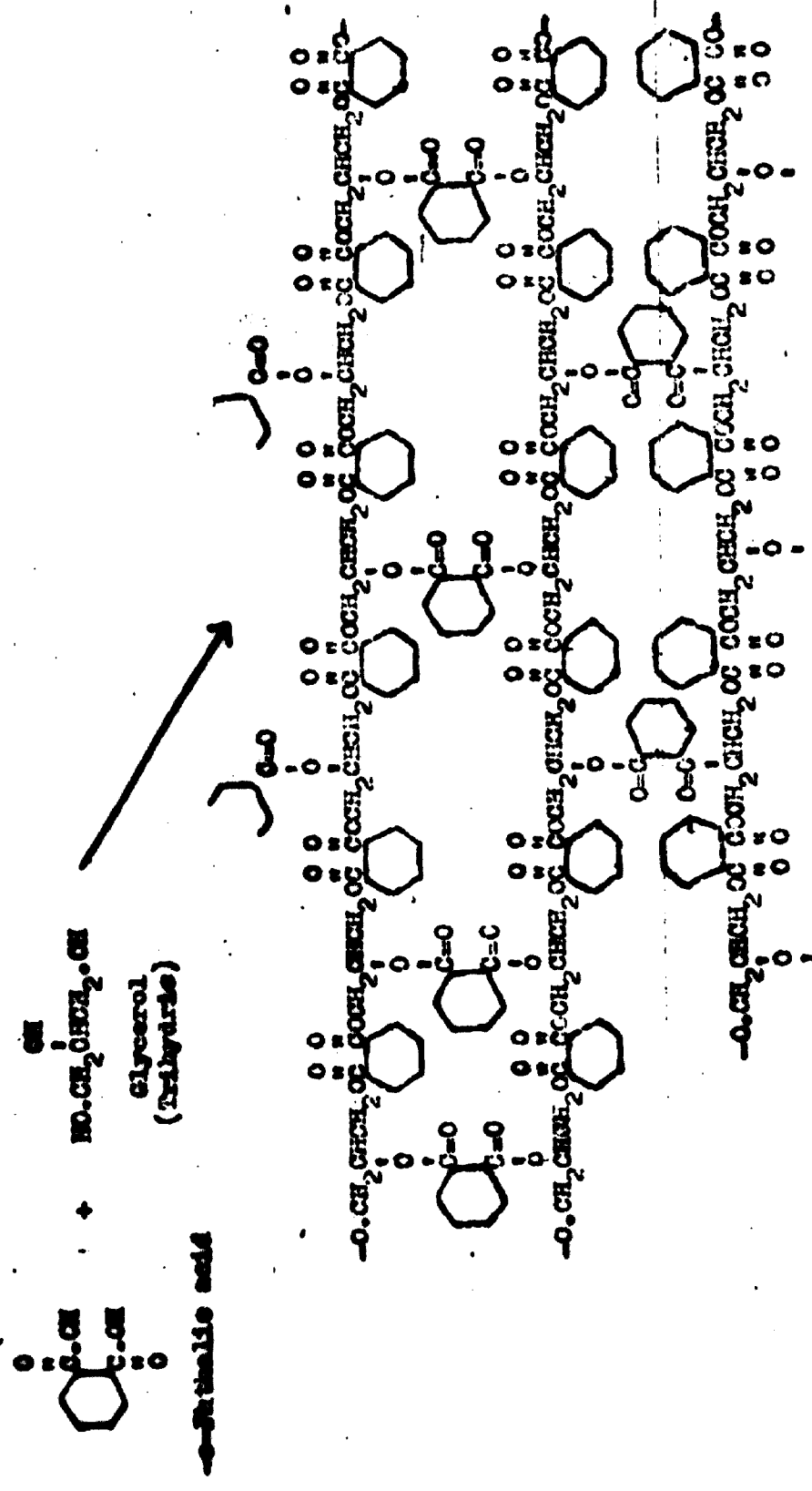
Case 2. Difunctional compounds react with Difunctional compounds to form Linear polymeric molecules



Cont'd.

Reaction 3a (cont'd)

Chem 3a. Multifunctional compounds react with trifunctional compounds to form Three Dimensional network polymers



**Glycerol-o-phthalate
(Thermosetting polymer)**

Although he demonstrated his postulates by esterification reactions between polyfunctional alcohols and acids, the principles apply irrespective of the nature of the functional groups. Furthermore reacting molecules may contain groups of mixed functionality. A molecule containing two groups of differing functionality capable of co-reacting with each other is, therefore, able to form polymers by head-to-tail reaction. This type of polymerization is exemplified by the formation of Nylon 6 from ϵ -caprolactam (See Diagram 2).

In the formation of thermosetting materials it is possible to select starting materials possessing functionalities of varying degrees of reactivity in order to produce linear molecules in the initial steps, which can subsequently be further reacted in order to effect cure or, in other words, cross-link to the three-dimensional state.

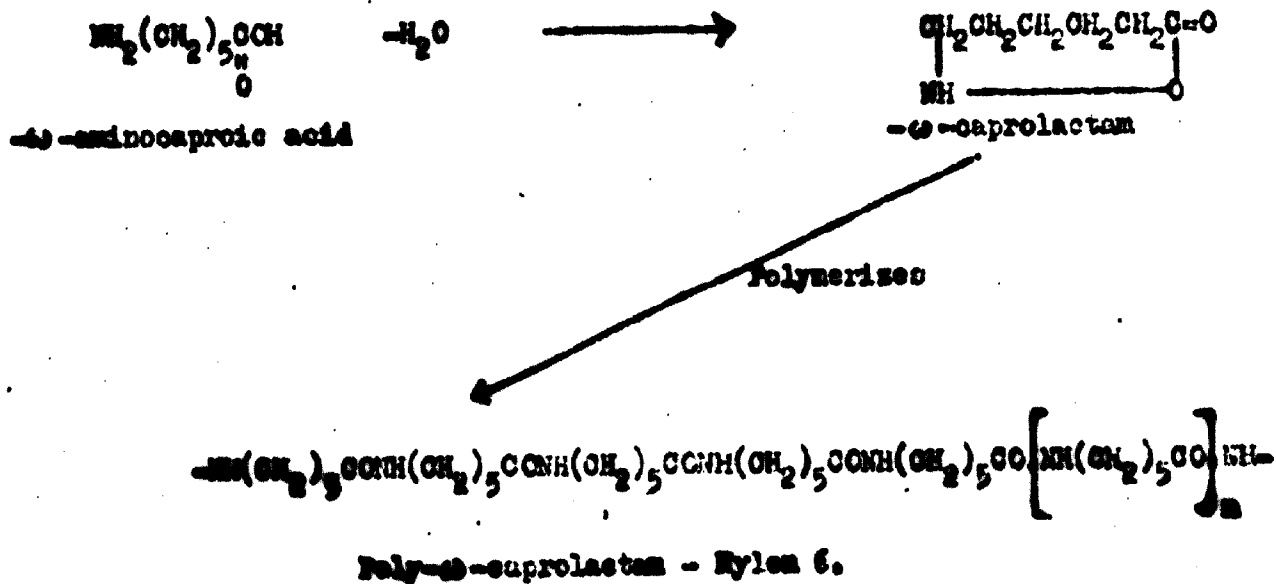
A further important classification arises from the nature of the reactive groups that give rise to functionality and the mechanisms whereby they react to form polymers.

Polymerization Reactions

The term polymerization refers to addition reactions that is linking without the evolution of by-products. This is conveniently illustrated only after a more detailed consideration of certain aspects of carbon chemistry: Carbon is tetra-covalent, that is to say an atom of carbon is capable of combining with four mono valent atoms or groups. In particular, Carbon atoms are capable of linking to form chain or ring structures. The simplest case of chain formation is that of the paraffin hydrocarbons (See Diagram 3). It will be noted that the number of carbon atoms in the chain has a direct bearing upon the physical properties of the molecule. Whereas in the case of the paraffin series of hydrocarbons all the valencies of the carbon atoms are fully satisfied by attached hydrogen atoms, a similar series of hydrocarbons, known as the olefines exists in which one pair of adjacent carbon atoms are deficient by two hydrogen atoms. The bond between these carbon atoms is said to be unsaturated or *Ethenoid*. Chains of four or more carbon atoms can

DIAGRAM 2.

MIXED FUNCTIONALITY



contain more than one unsaturated group and if two unsaturated groups are located between adjacent pairs of carbon atoms the unsaturation is said to be conjugated and possesses high reactivity. Certain hydrocarbons containing conjugated unsaturation are the basic monomers for the production of many of the synthetic rubbers.

Each ethenoid bond is difunctional and capable of undergoing polymerization terminal ethenoid bonds having greater reactivity in this respect than ethenoid bonds positioned towards the centres of molecules. In certain circumstances the terminal ethenoid group is known as a *vinyl group*. This is exemplified by the greater difficulty experienced in effecting polymerization of such compounds as 3,4-butene.

While the polymerization of unsaturated hydrocarbon groups forms the basis of most of the well-known thermoplastics other groups are capable of undergoing addition reactions by rearrangement of their constituent atoms. This most commonly occurs by the fission of strained rings as in the case of the epoxide resins or weak bonds in rings as in the case of Nylon 6 formation.

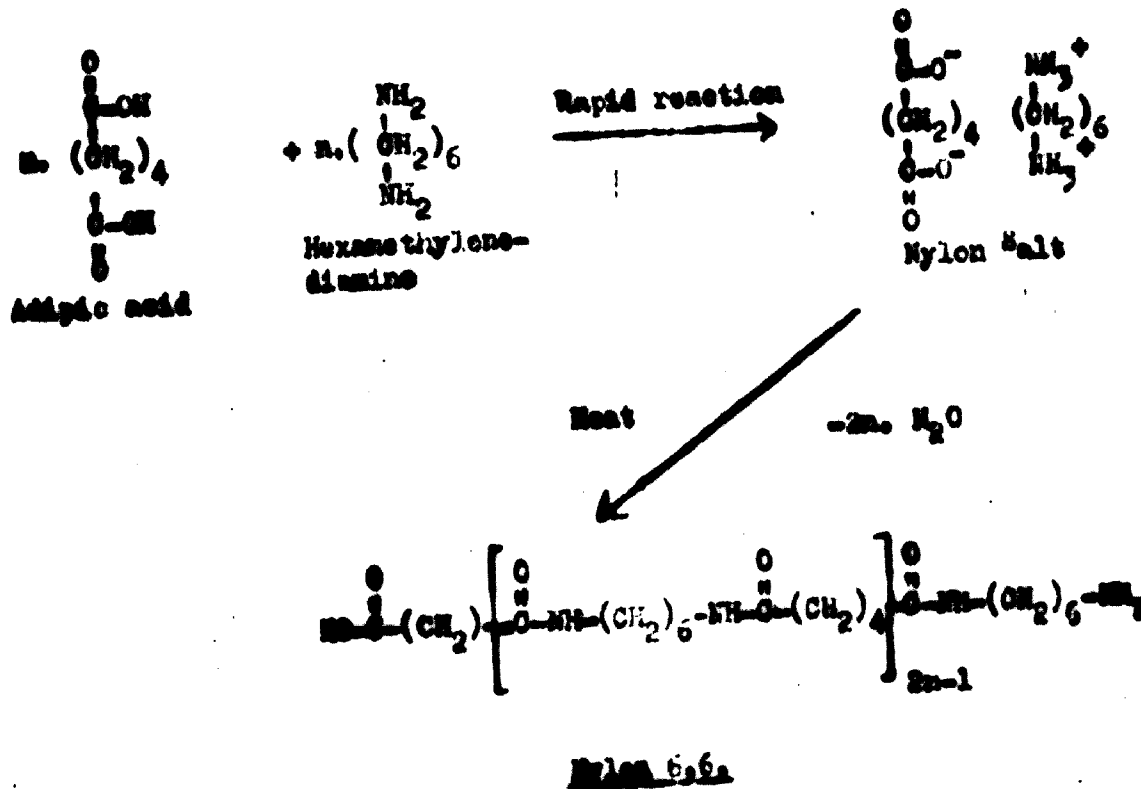
Polycondensation Reactions

If a compound A reacts with a compound B to form product C by elimination of water, or other low molecular weight by-products, the reaction is said to be that of condensation. The simplest condensation reaction is perhaps the elimination of water between an acid and an alcohol to form an ester. This process being analogous to that of salt formation in the field of inorganic chemistry but, whereas in salt formation the reaction occurs spontaneously on mixing, esterification is brought about only by the positive removal of water between the acid and alcohol.

In the manufacture of the nylons we have an example of initial salt formation between organic bases (diamines) and diacids followed by elimination of water from the salt to form the polymer. Salt formation occurring on mixing the two ingredients and condensation occurring only on heating at high temperature. (See Diagram 4).

DIAGRAM 4.

SALT FORMATION AND POLYCONDENSATION



Of major importance in the synthesis of thermosetting resins is the reaction of aldehydes, particularly formaldehyde, with a variety of polyfunctional compounds to form methylol groups which can subsequently co-react by condensation to cause molecular growth.

Although the major classification of synthetic polymers is derived from structural considerations and reaction types further sub-classification derives from such factors as:

The chemical class and nature of the starting materials
(building bricks)

In the case of polymerization products:

- a. The type of unsaturation in the monomer, in particular polymers derived from monomers containing conjugate unsaturation such as butadiene, form the basis of the synthetic rubbers.
- b. Whether a single monomer is employed to form a Homopolymer or whether a plurality of different monomers are employed to give Co-polymers which may, for example, be binary or ternary.
- c. Whether substituent groups in the polymer chain are randomly directed (atactic), all directed in the same way in respect of the polymer chain (isotactic) or directed alternately in groups in different but regular directions (syndiotactic).
- d. By physical characteristics, in particular, the extent of crystallinity a factor very much influenced by c. above.
- e. The physical state in which the polymerization reaction has been effected, viz. bulk, solution, suspension or emulsion.

In the case of polycondensation products:

- a. The nature of the condensation reaction.
- b. The chemical type of starting material e.g. phenolic, aminoplast, urethane etc.
- c. Whether or not the product is curable.
- d. The nature of its properties for example, oil solubility, adhesive characteristics, chemical resistance.
- e. Structure of the cured product, particularly in terms of its end use such as - composite, foam or cast.

Paper 2

THERMOPLASTIC SYNTHETIC POLYMERS

By far the highest proportion of products within this group are those derived by polymerization, of these the following are of major importance:

Polyvinyl Chloride, and vinyl chloride co-polymers.

Polystyrene, styrene co-polymers and styrene based polymer blends.

Polyolefines.

Polymethyl methacrylate and acrylics.

Polyvinyl esters and derived products.

Before discussing these individually it is advisable to briefly discuss plasticization.

While certain plastics possess an inherent flexibility others may suffer from such disadvantages as brittleness, excessive stiffness at the temperatures which have to operate during the forming stages of processing, lack of resistance to fatigue, internal stresses. In order to offset these disadvantages plasticization is frequently necessary and plasticization methods may be fall into the following classes.

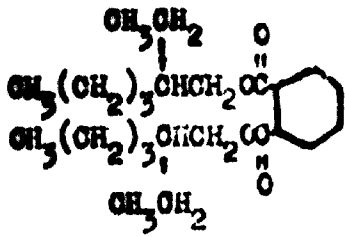
External Plasticization

Involves the incorporation into the polymer of a non-volatile plasticizer which is mutually compatible therewith.

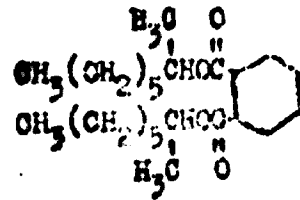
Such plasticizers may be either high boiling compounds such as phthalates of C_4 to C_{12} alcohols, the commonest being Di Octyl phthalate (DOP) which is in fact di 2-ethyl hexyl phthalate and Di isooctylphthalate (DIOP) which are the general purpose plasticizers for PVC. Secondly, come the phosphate plasticizers such as tricresyl phosphate which in addition tends to confer a degree of fire-retardance, then the esters of the saturated aliphatic di acids such as the adipates and sebacates, which are particularly useful in conferring low temperature flexibility. Relatively low molecular weight polyesters of adipic and sebacic acids with ethylene or propylene glycols are also used, especially when a high degree of resistance to migration is required. (See Diagram 5).

DIAGRAM 5.

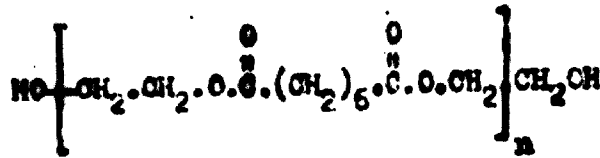
PLASTICIZERS



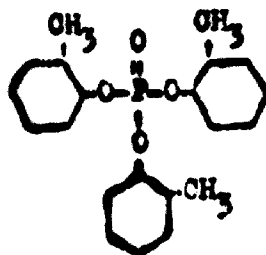
Di-n-butylphthalate
D.B.P.



Di-isooctylphthalate
D.I.O.P.



Polyethyleneglycol sebacate



Triresyl phosphate

Internal Plasticization

Effected by introducing a flexibilizing etc. co-monomer prior to polymerization.

A classic example of this technique is given by the use of vinyl chloride-vinyl acetate co-polymer, containing about 5% vinyl acetate in order to ensure adequate flow to give exact reproduction in the manufacture of micro-grooved gramophone records.

Polymer Blending

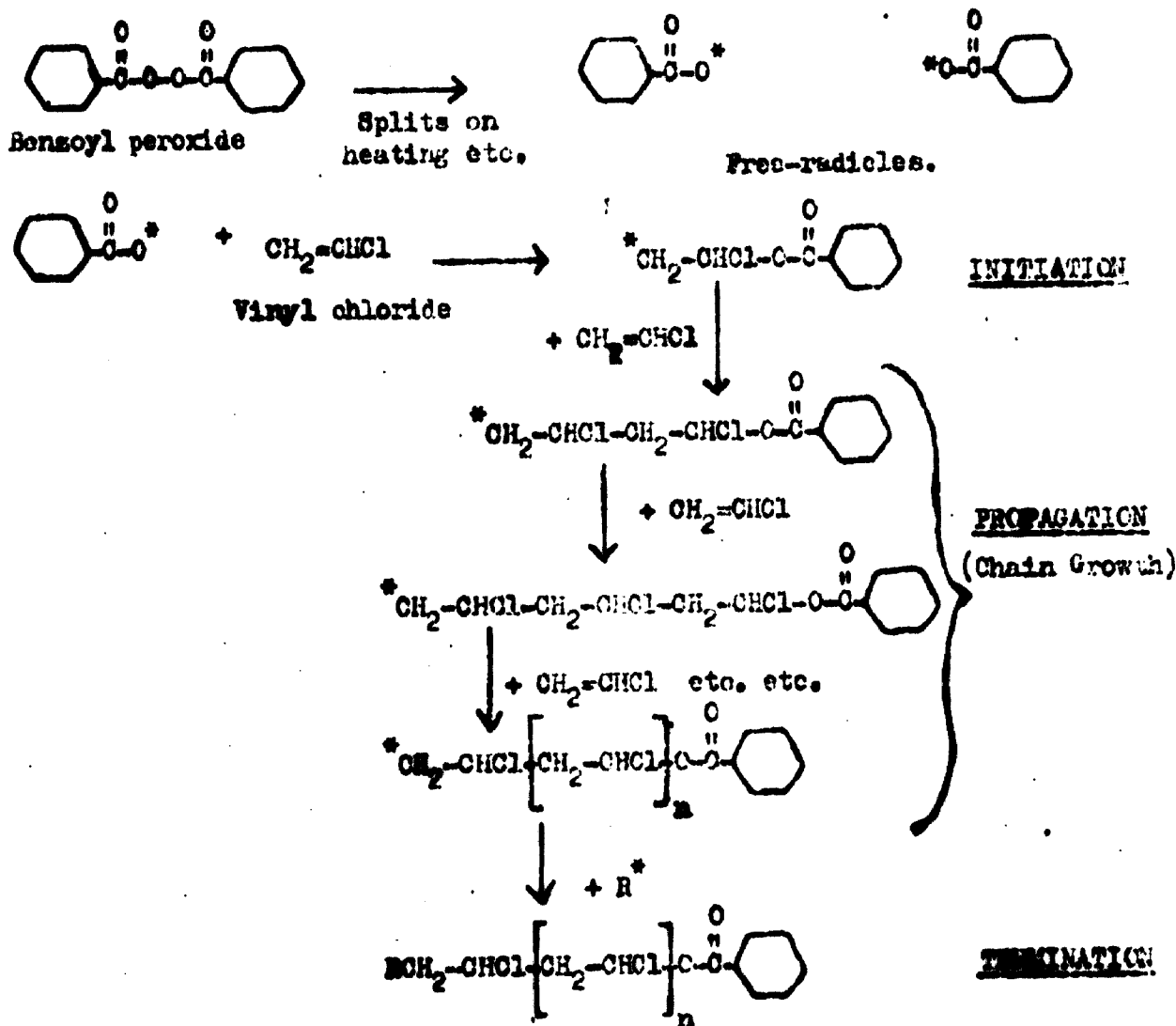
Polymers such as polystyrene cannot be effectively plasticized by conventional plasticizers, which reduce their hardness and increase their thermo-softening characteristics. Thus in order to enhance its impact strength plasticization is effected by blending with compatible rubbers, in particular butadiene-styrene rubbers. This is effected either by direct blending in an extruder-blender or by overcoating a butadiene styrene co-polymer latex with in-situ polymerized styrene.

POLYMERIZATION

The subject of polymerization is exceedingly broad and, owing to space limitations, can only be dealt with in outline. Polymerization of unsaturated compounds is normally effected catalytically. Catalysts being of the free-radicle, ionic or Friedel-Crafts type. For simplicity the basic mechanism of free-radicle catalysis is outlined in Diagram 6. The commonest free-radicle catalysts are organic peroxides or hydroperoxides. At the initiation stage the catalyst splits into two free-radicles each of which can open the unsaturated group by addition to one carbon atom, the active centre being

DIAGRAM 6.

FREE-RADICAL POLYMERIZATION



Where Free-Radicle R^* may be:

1. Another catalyst fragment
2. An active centre on another growing chain which, if in a terminal position causes doubling or, if in the body of the chain causes branching.
3. An impurity.

Or R^* may be a proton (Hydrogen atom or ion), for example, introduced in the form of a chain transfer agent (Proton donor) such as decyl mercaptan, to control molecular weight.

transferred to the other carbon atom in the group. This moiety then functions as a free-radicle and as chain growth proceeds the active centre is transferred along the chain to a terminal position. This stage is known as Propagation. Termination of chain growth can occur only neutralization of the active centre by one of the conditions described in the diagram.

Polymerization may be effected in any of the following ways:

1. Bulk Polymerization - In which the monomer is undiluted.
2. Solution polymerization - In which case the solvent may be selected either so that:
 - (a) The monomer is soluble and the polymer is insoluble.
 - (b) Both the monomer and polymer are soluble.
3. Suspension Polymerization - In which the monomer is suspended in water with slow stirring, in the form of droplets, by means of a protective colloid, to give a polymer in the form of spherical beads.
4. Emulsion Polymerization - The monomer is emulsified in water, by means of an emulsifying agent (soap) and a protective colloid and then polymerized to a latex.
5. Heterogeneous Polymerization - In which the catalyst is in a separate phase from the monomer e.g. A gaseous liquid monomer in contact with a solid catalyst.

MAJOR THERMOPLASTICS PRODUCED BY ETHENOID POLYMERIZATION

1. Vinyl Chloride etc. Polymers (Diagram 7)

This class includes PVC itself, by far the most important, vinyl chloride-acetate co-polymers and polyvinylidene chloride.

PVC is normally produced by emulsion polymerization using a peroxide catalyst. As the monomer is gaseous at normal

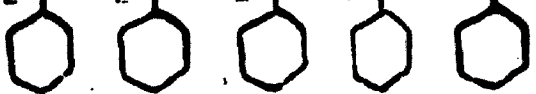




DIAGRAM 7.

MAJOR POLYVINYL HALIDES

		Monomer.
Polyvinyl chloride (PVC)	$-\text{CH}_2-\text{CHCl}-\text{CH}_2-\text{CHCl}-\text{CH}_2-\text{CHCl}-\text{CH}_2-\text{CHCl}-$	$\text{CH}_2=\text{CHCl}$ Vinyl chloride.
Polyvinylidene chloride (PVDC)	$-\text{CH}_2\text{CCl}_2-\text{CH}_2-\text{CCl}_2-\text{CH}_2-\text{CCl}_2-\text{CH}_2-\text{CCl}_2-$	$\text{CH}_2=\text{CCl}_2$ Vinylidene chloride
Polytetrafluoroethylene (PTFE)	$\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{CF}_2-$	$\text{CF}_2=\text{CF}_2$ Tetrafluoroethylene

DIAGRAM 8.

MAJOR STYRENE POLYMERS

Polystyrene	$-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-$ 	$\text{CH}_2=\text{CH}$  Styrene.
Styrene-butadiene co-polymer.	$-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-$ 	Styrene + $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ Butadiene.
Acrylonitrile-butadiene-styrene co-polymer (ABS)	$-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}-$  CN	Styrene, butadiene + $\text{CH}_2=\text{CH.CN}$ Acrylonitrile.
Methyl methacrylate-butadiene-styrene co-polymer (MBS)	$-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{C}-$  $\begin{matrix} \text{CH}_3 \\ \\ \text{C} \\ \\ \text{O}=\text{O} \\ \\ \text{C}-\text{OH}_3 \end{matrix}$	Styrene, butadiene + $\begin{matrix} \text{CH}_3 \\ \\ \text{CH}_2=\text{C} \\ \\ \text{O}=\text{O} \\ \\ \text{C}-\text{OH}_3 \end{matrix}$ Methyl methacrylate

pressures reaction is effected in pressure vessels. PVC is characterised by its horn-like qualities in unplasticized (or rigid) state and its capacity to tolerate a wide range of plasticizer concentration i.e. up to at least 48% to give a wide variety of products of varying degrees of flexibility and extensibility from rigid to rubbery gels.

Vinyl chloride acetate co-polymers (already discussed) are produced in a similar manner to that of PVC and are used in various applications ranging from adhesives and coatings to moderately rigid products (some bottles) where enhanced flow during fabrication is demanded. The co-polymer of vinyl chloride with vinylidene chloride (PVDC) is tough with very good flexibility and has superior heat resistance to PVC is most commonly known as *Saran* in the form of extruded threads used in the manufacture of exterior upholstery (Deck chair etc. canvas)

The main disadvantage of PVC lies in its lack of resistance to heat and U-V light, for this reason the incorporation of stabilisers - metal soaps etc. for heat stability and polyphenols etc. for U-V stability is invariably practiced.

2. Polystyrene (Diagram 8)

Styrene polymers and co-polymers form a very important group of materials whose applications range from the widely recognised crystal clear rigid mouldings through to the synthetic rubber GR-S, this range includes:

Polystyrene produced by bulk polymerization in the presence of free-radicle catalysts. Moulding powders (crystal) being compounded with soluble dyestuffs extruded and cut into pellets. Suspension polymers are also produced but have not the same degree of clarity as the bulk polymerized material. One interesting class of suspension polymer are the beads produced

for foaming. In this case the monomer is mixed with the foaming agent (a low-boiling solvent such as pentane) and catalyst dispersed in water containing a suspending agent, usually polyvinyl alcohol stirred to form the suspension and polymerized in the form of spherical beads. While polystyrene can be emulsion polymerized this is not usually done as the particles do not coalesce to form a film on drying, unless plasticizers are added, which tend to cause tackiness and detract from its thermal properties. High impact Polystyrene is generally produced by emulsion polymerization onto a synthetic rubber (GR-S) latex.

Styrene Co-polymers

The most important of these are:

ABS - a ternary co-polymer of styrene, butadiene and acrylonitrile used extensively in the manufacture of extruded sheet for vacuum forming. Styrene-butadiene co-polymer - in which the styrene preponderates e.g. app. 62.5% styrene, 37.5% butadiene which is used in the manufacture of semi-hard rubbers as a modifier. Styrene-butadiene co-polymer in which the butadiene preponderates e.g. butadiene 62.5% + styrene 37.5% - for the important group of GR-S synthetic rubbers. The general purpose replacement or extender for natural rubber.

3. Polyolefines (Diagram 9)

This group of polymers comprises mainly: The polyethylenes (High and Low density) and polypropylene and more recently Poly 4-methyl pentene -1 (TPX-I.C.1) - Polyethylene - Low Density - This inherently flexible polymer is produced by the polymerization of ethylene

at high pressure; approx. 2,000 p.s.i.; in the presence of a free-radicle catalyst.

Polyethylene - High Density - During the early 1950's Karl Ziegler discovered that ethylene could be polymerized at low pressure in the presence of modified Friedel-Crafts catalysts based upon combinations of aluminium alkyls and mixed Titanium chlorides (Ti^{3+} and Ti^{4+}) to give a polymer which was harder, more rigid and of higher density than the conventional polyethylene (i.e. app. .96 to 0.93). It rapidly found application in mouldings, film and sheet and particularly in hollow, blow moulded containers.

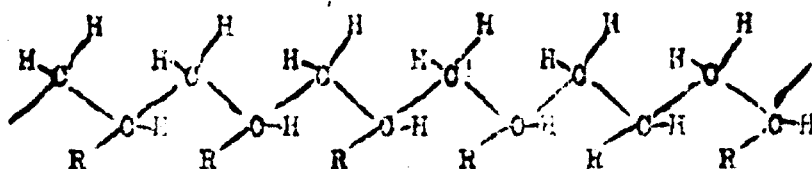
The difference in properties between the two materials is primarily due to the fact that because of the method of polymerization the LD material contains a high element of branched chains and is consequently substantially non-crystalline in its nature i.e. because of the chain branching the molecules do not pack as closely as those of the unbranched material and are consequently less susceptible to orientation on drawing or passage through narrow orifices during extrusion.

Polypropylene - Practically simultaneously with the work of Ziegler, Natta in Italy discovered that similar catalysts had the capacity to influence the path of polymerization to effect isotacticity and the propylene could be polymerized in such a manner that the pendent methyl groups remained on the same side of the polymer chain. Because of this factor the molecules in polypropylene are highly regular and PP is characterised by its high crystallinity. This characteristic is exploited in many ways, particularly in fibrillated

DIAGRAM 10.

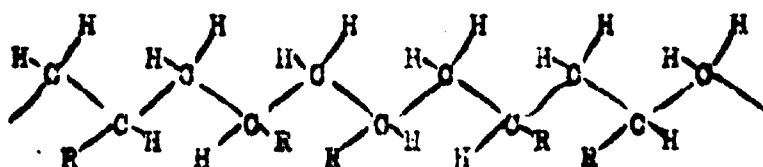
TACTICITY.

ISOTACTIC (Same spatial direction)



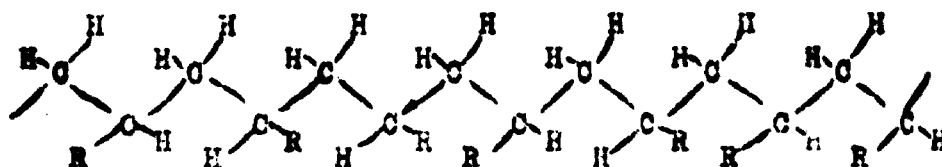
If the lower C atoms are visualised as lying in the plane of the paper all the substituent R groups will lie above it.

SYNDIOTACTIC (Regular spatial direction)



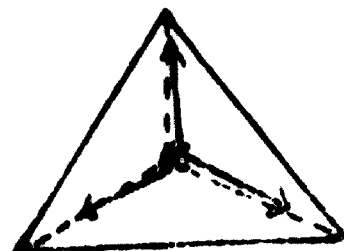
If the lower C atoms are visualised as lying in the plane of the paper alternate R groups (or regular blocks of R groups) will lie above and below it.

ATACTIC (Random spatial direction)



If the lower C atoms are visualised as lying in the plane of the paper the substituent R groups lie randomly above and below it.

Note: The bonds of the carbon atom are directed towards the corners of a regular tetrahedron, thus:



films, fibres and so-called *Living hinges*. The concept of tacticity, which is of particular importance not only to the understanding of the polyolefines but also of the behaviour of many elastomers, is shown in Diagram 10.

4. Acrylics (Diagram 11)

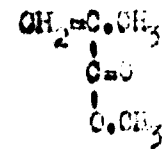
Acrylic polymers are derived from esters of acrylic acid or substituted acrylic acid, in particular esters of methacrylic acid, the most important monomer being methyl methacrylate.

Polymethyl methacrylate - During the 1930's I.C.I. invented the process of bulk polymerizing MMA between sheets of glass to produce the clear, tough plastic sheet known as *Perspex*. Although PMMA is capable of withstanding temperatures up to that of boiling water without significant distortion, it is readily thermo-formable at temperatures just above 100°C. and can be shaped with simple tools prepared from cheap materials such as wood. In the unmodified state bulk polymerized PMMA is difficult to adapt to the injection moulding process. Injection moulding grades of PMMA can, however, be produced by modifications introduced during the polymerization process in order to improve flow characteristics, typical of these is the introduction of chain transfer agents to control molecular weight. The combination of clarity and impact strength of PMMA mouldings is exploited by their use in the manufacture of automotive lighting lenses. Further modifications can also be effected to produce special purpose grades of sheet in order to achieve, for example, improved standards of fire-retardance. Grades of cast polymer, capable of undergoing further heat cure may be produced by the introduction of polyfunctional co-monomers such as allyl methacrylate.

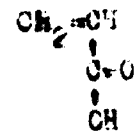
DIAGRAM 11.

MAJOR ACRYLIC POLYMERS

Monomers:

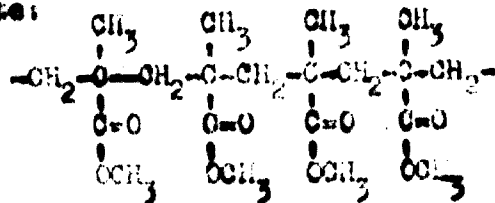


Methylmethacrylate



Acrylic acid.

Polymethylmethacrylate:



Polyacrylic acid:

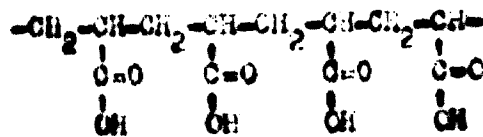


DIAGRAM 12.

MODIFYING ACRYLIC MONOMERS

Promoters:

Flexibility

Solubility in organic solvents and compatibility with resins.

Flexibility and compatibility

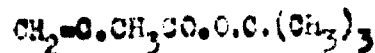
Cureability by polymerization.

Water solubility - ionic-like salts.

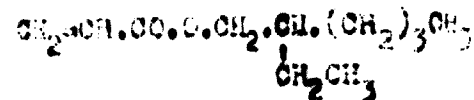
-n-Butyl acrylate



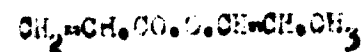
-t-butyl methacrylate



2-ethylhexylacrylate



Allyl acrylate



Acrylic acid



Acrylic Co-polymers - Of rapidly increasing importance in the surface coatings field, binary and ternary co-polymers embodying various groupings are produced to give virtually tailor made properties. Basic effects being imparted according to the substituent group in the monomer as follows:

Acrylic esters More flexible than Methacrylic esters
Free acids (viz acrylic acid and methacrylic acid) - water soluble.

Alcoholic Group		Hydrocarbon Radicle
Methyl	Rigid	1 C atom
Butyl-n-	Flexible	4 C atom
Butyl-t-	Less than -n- but improved solubility characteristics	4
Octyl (2-ethyl hexyl)	Highly flexible	8

These are summarised. (Diagram 12)

5. Polyvinyl Acetate (Diagram 13)

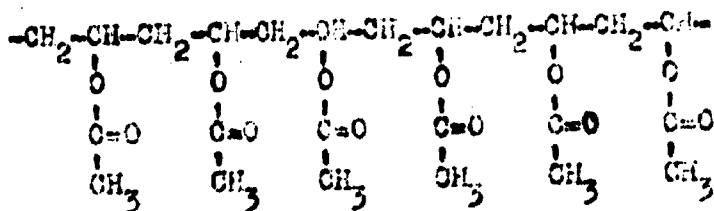
Originally bulk polymerized PVAc was produced in the form of a moulding powder (Gelva), largely owing to its low softening temperature and relatively poor water resistance this has now been superseded by other moulding materials. Emulsion polymerized PVAc has, however, assumed considerable importance both as a surface coatings binder and in the formulation of adhesives. Perhaps, however, the most interesting application of PVAc is in its use as an intermediate in the production of Polyvinyl Alcohol (PVA or PVOH). This is a water soluble polymer which finds application in the following fields:-

- i. As a protective colloid (suspending agent).
- ii. In the production of water-soluble fibres and films, which can be insolubilised by

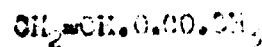
DIAGRAM 13.

POLYVINYL ACETATE AND ITS DERIVATIVES

POLYVINYL ACETATE:

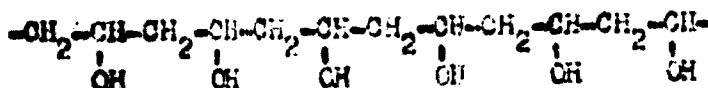


Monomer.



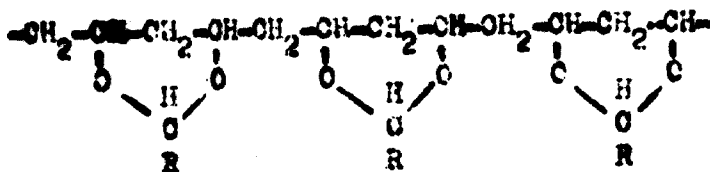
Vinyl acetate.

Alkaline or
acid
Hydrolysis



POLYVINYL ALCOHOL

Treatment with
aldehydes: -
Acetalation.



Where R = H the resulting polymer is POLYVINYL FORMAL
 " " = CH₃ " " POLYVINYL ACETAL
 " " = C₂H₅ " " POLYVINYL BUTYRAL

by reaction with, for example, formaldehyde.

- iii. As an intermediate in the production of the polyvinyl acetals by reaction with various aldehydes the principle aldehydes involved being:

Formaldehyde - to produce polyvinyl formal - used in adhesives.

Acetaldehyde - Polyvinyl acetal - declining in use.

Butyraldehyde - Polyvinyl butyral - used in safety glass interlayers, insulating varnishes etc.

MISCELLANEOUS POLYMERS (Diagram 14)

Polyoxymethylenes - These are stable polymers of very pure formaldehyde manufactured initially by Du Pont under the trade name *Delrin*. They are hard and tough with excellent abrasion resistance and can be moulded to high precision.

Polycarbonates - e.g. *Makrolon* - Farbenfabriken Bayer.

These are an example of polymers which embodied aromatic elements in the chain itself and in consequence have significantly higher softening ranges than those polymers already considered. In addition they are colourless and possess excellent clarity. They are used in a range of applications including exterior light fittings (street lights) and sterilizable items such as babies feeding bottles. They are produced by the reaction of bisphenol A, (bis 4-4' -dihydroxy-dibenzyl-propane) with phosgene (COCl_2).

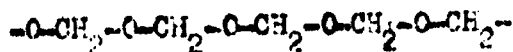
Polyethylene terephthalate

This linear aromatic polyester, discovered by Winfield & Dixon is better known as the synthetic fibre *Terylene*. Its use in the fibre form (Mellinex) has increased very sharply over the last 10 years because of the combination of very high strength, clarity and flexibility it possesses.

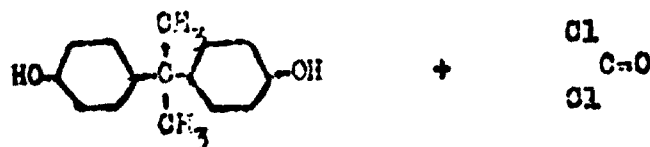
DIAGRAM 14.

MISCELLANEOUS POLYMERS

POLYOXYMETHYLENE (Polyacetal) - Produced by polymerization of pure formaldehyde.

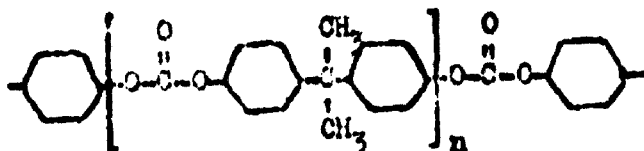


POLYCARBONATE Produced by the phosgenation of Bisphenol A.

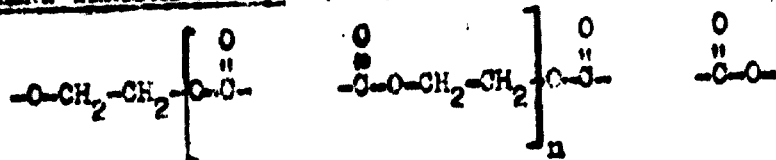


Bisphenol A.
(*Res-4-hydroxy-*
diphenylpropane)

Phosgene.

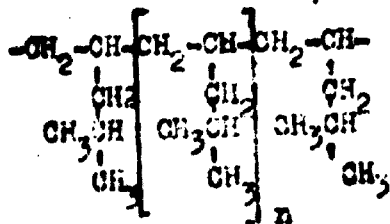


POLYETHYLENE TEREPHTHALATE (Polyester - Melinex, Terylene etc.)

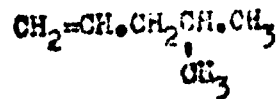


Produced by polycondensation of ethylene glycol and terephthalic acid.

POLY-4-Methylpentene-1 - TFX. An isotactic polyolefine produced by Zeigler-Natta polymerization.



Monomer:



4-Methylpentene-1

Particularly as a result of the demands of the aerospace and aviation industries much development has been directed towards obtaining polymers of progressively higher softening ranges. Much work has been done on the preparation of polymers embodying inorganic elements in their chains. With the exception of the Silicones, this work has not been highly successful and the emphasis has now been switched to the production of a wide range of polymers embodying highly aromatic chains, e.g. polypyromellitic acid and polypyromellitides.

THERMOSETTING SYNTHETIC POLYMERS

Whereas the majority of thermoplastics are recognised as such, mainly because they are directly employed in the manufacture of finished articles with relatively little modification, thermosetting resins on the other hand are frequently so modified that they tend to lose their identity in that of the finished product. For example, it is easy to recognise a glossy table cloth as *Plastic* but an abrasive wheel bonded by means of a phenolic resin is rarely, if ever, associated with plastics. Thus it is possible to regard the thermosets as the submerged section of the plastics iceberg.

The broad scope of the application of the more important thermosets is outlined in Diagram 15.

The largest class of thermosets, which have the broadest application of all plastics materials, is that of the aldehyde condensation products, the applications of many of these pre-dating those of the non-cellulosic thermoplastics. These products are based upon the capacity of aldehydes to combine with chemical groups containing active hydrogen atoms to form methylol or substituted methylol groups which, in turn condense with each other or with other active hydrogen atoms to form methylene or substituted methylene linkages. The active hydrogen atoms with which the aldehydes react are principally located as follows:

- (a) When benzene (cyclic C_6H_6) is substituted by a hydroxyl group (phenol) this group activates the reactivity of the hydrogen atoms in the positions ortho and para to it. An amino group behaves in a somewhat similar manner to the hydroxyl group but the aniline-aldehyde resins have never achieved the commercial significance of the phenolics.
- (b) The hydrogen constituents of amino groups themselves are reactive towards aldehydes, particularly when they are enhanced by the presence of an adjacent unsaturated bond, such as occurs in urea with the carbonyl group or melamine with unsaturation within the triazine ring.

DIAGRAM 15.

CLASSIFICATION AND BREADTH OF APPLICATIONS OF MAJOR THERMOSETS

1. ALDEHYDE CONDENSATION PRODUCTS

- a) Phenolic Resins
- b) Aminoalant Resins
- c) Miscellaneous

Moulding powders; paper, fabric and glass fibre laminates; adhesives; insulating materials, sealing compounds, abrasive products including rigid forms; hardness modifiers for rubbers; marine varnishes; polishes; oxide resin hardeners; and industrial binders for use in many fields including abrasives, friction materials, foundry sands and cork composition.

2. POLYESTER RESINS

- a) Unsaturated Polyesters
- b) Oil Modified Alkyds

Reinforced plastics; coatings; adhesives and surface coatings.

3. EPOXIDE RESINS

- a) Epoxide Resins
- b) Epoxy Esters

Reinforced plastics; coatings; adhesives, chemically resistant surface coatings for plant, floorings, road paints etc.

4. POLYURETHANES

- a) Polyester based.
- b) Polyether based
- c) Amine based

Synthetic rubbers; coatings; adhesives; surface coatings, rigid and flexible forms.

These two types of activation lead to the two major groups of aldehyde resins, namely the phenolics and the aminoplasts. It is proposed to consider the chemistry of the phenolics in somewhat greater detail than the other thermosets as this presents a considerably clearer picture of the types of reaction involved.

PHENOLIC RESINS

The basic chemistry of phenolic resin formation is presented in Diagrams 16 and 17. The fundamental difference between the single stage resins (Resoles) and the two stage resins (Novolaks) is entirely dependent upon the instability of the methylol group under acidic conditions. If the initial reaction is effected with acid catalysts the methylol groups condense so rapidly that control cannot be effected thus if the amount of aldehyde is sufficient, gelation inevitably occurs prematurely.

In the formulation of phenolic resins, in addition to the use of or modification by the phenol and aldehyde variants shown in Diagrams 18 to 20 other major variations may be effected as follows:

1. Resoles

(a) Formaldehyde ratio.

Generally the minimum amount of combined formaldehyde necessary to achieve cureability is slightly less than 0.9 molar. As this ratio is exceeded, yields improve and cure is accelerated up to about 1.5 molar.

Higher aldehyde ratios are employed in the formulation of cold-curing adhesives which harden under the influence of acid catalysts such as hydrochloric acid or para toluene sulphonic acid and in the manufacture of cast phenolic resins ratios of up to 2.5 molar are frequently employed.

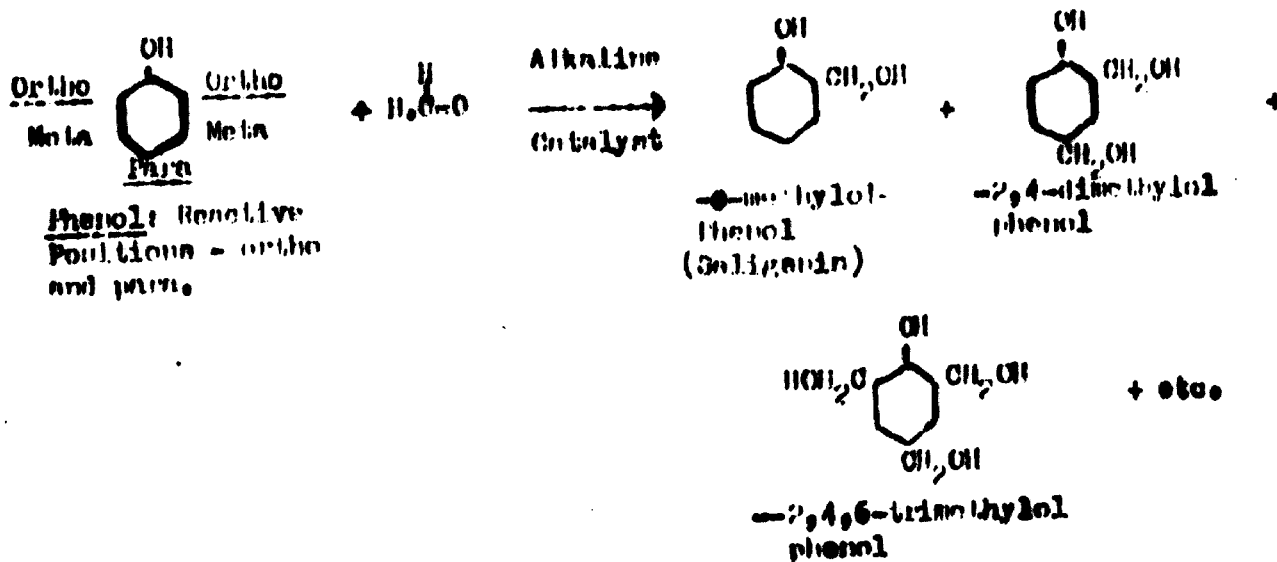
(b) Catalyst.

While the normal catalyst for resole manufacture is sodium hydroxide other basic catalysts are used to obtain special effects, these include:

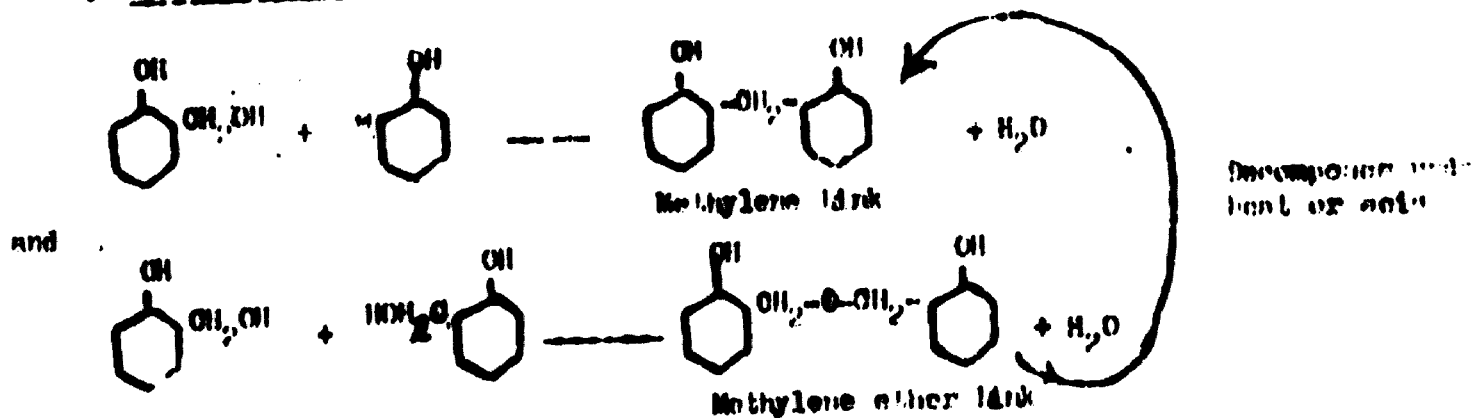
DIAGRAM No. 16

SINGLE STAGE PHENOLIC RESINS - IDEALS

1. Initial Reaction - METHYLATION



2. CONDENSATION Reactions

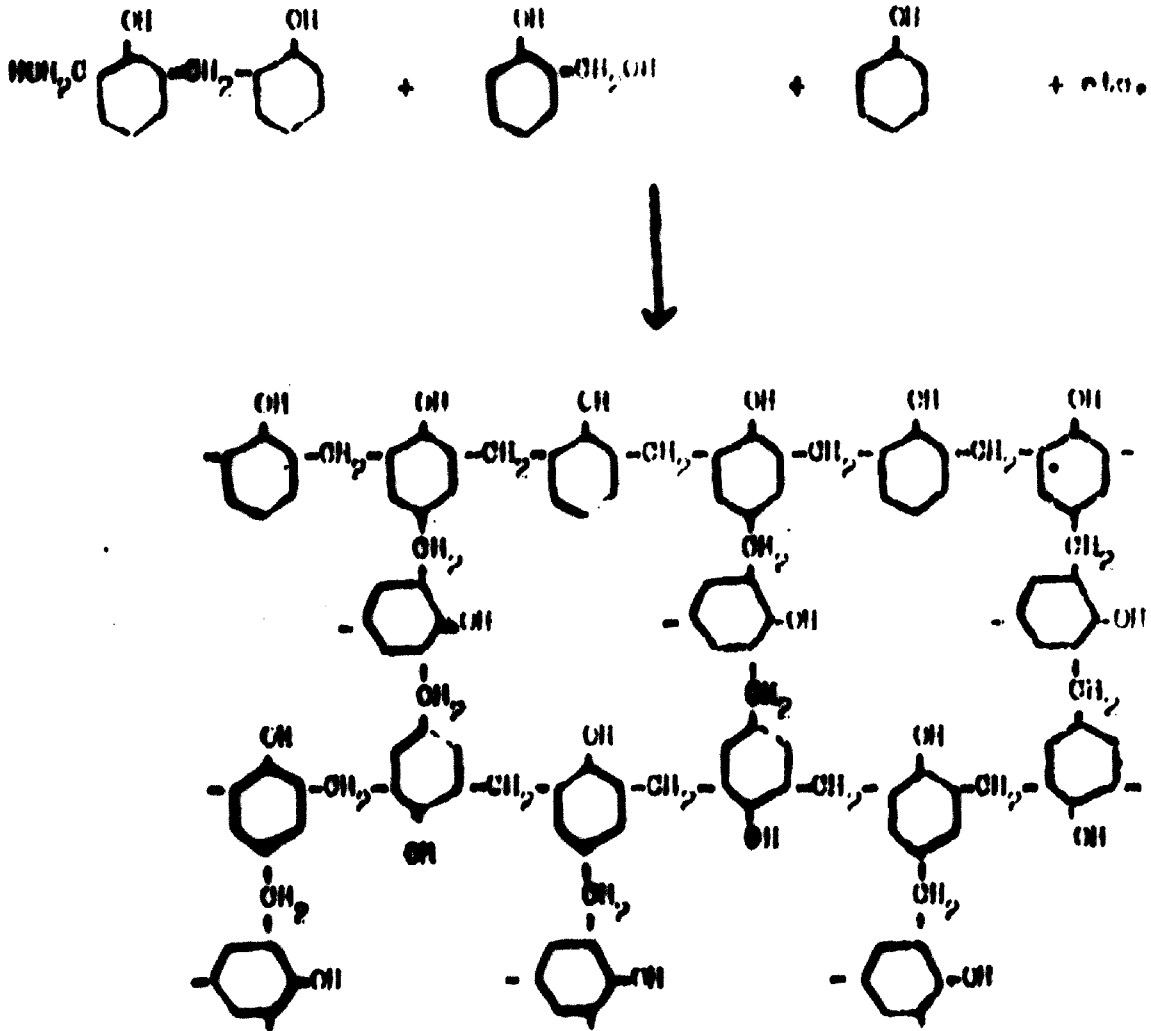


Generally the early stages of condensation occur to varying degrees simultaneously with methylation to produce a liquid product of syrupy consistency - This product is known as 'Stage'.

Continued

Chapter 16, Cont'd.

3. GEL FORMATION AND CURE

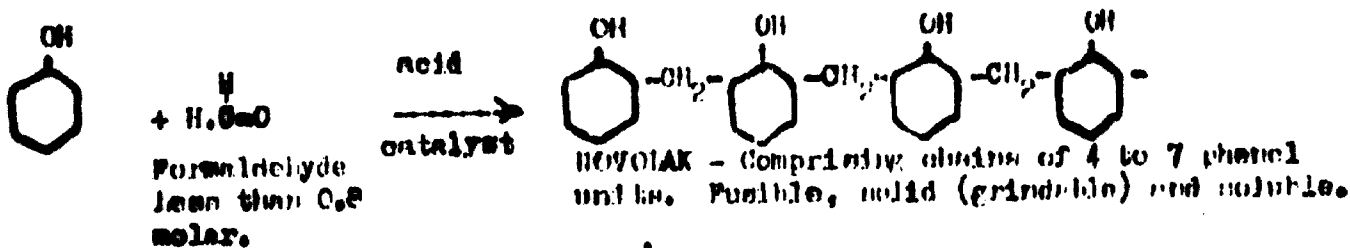


As condensation proceeds, on further heating, molecular growth gives rise to progressively increasing viscosity until gelation occurs. This is known as 'B Stage'. Further condensation continues until the resin is fully cured to the insoluble-infusible state, 'C Stage'. The cured resin is known as a Resite or Resitol.

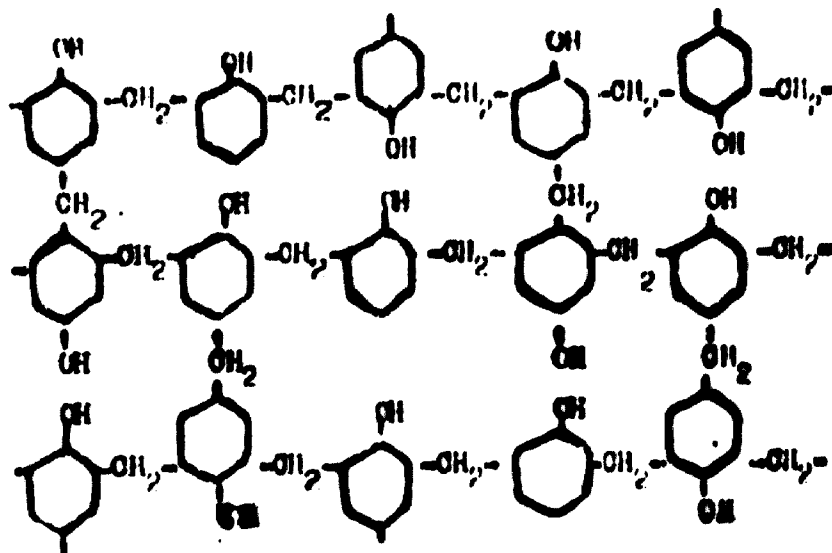
DIAGRAM 17.

TWO STAGE PHENOLIC RESINS - NOVOLAKS

First Stage:



Reacts with an aldehyde or aldehyde donor.



ALDEHYDE DONORS

Most commonly used - Hexamethylene tetramine (Hexa)



Decomposes on heating at 125°C. +

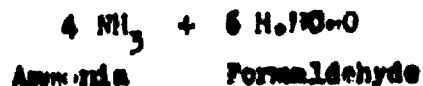


DIAGRAM 18

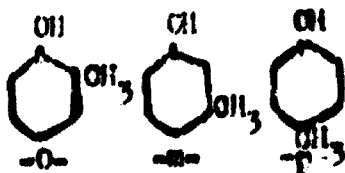
PHENOL VARIANTS AND THEIR APPLICATIONS

1. General Purposes:



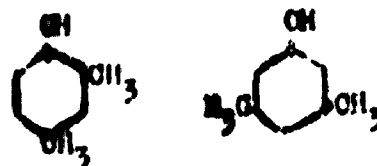
Phenol

Cheapest
general purpose



ortho, meta and para
cresols

Increasing source-reserved for electrical applications
(From coal tar distillation)

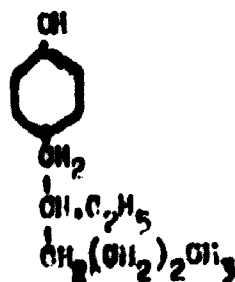


2,4-xyleneol 3,5-xyleneol
and other isomers.

2. Para Substituted Phenols - For compatibility with drying oils and synthetic rubbers i.e. marine varnishes and adhesives, etc.



-p-tertiary-
butyl phenol



-p-tertiary octyl
phenol

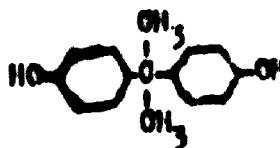


-p-phenyl phenol

3. Dibasic Phenols



Resorcinol
Very reactive for
cold-curing resins

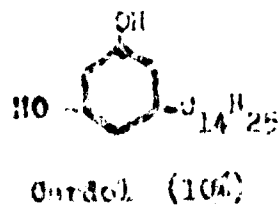
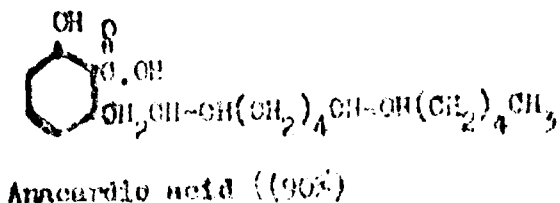


Bisphenol A.
-4,4'-dihydroxyphenyl-
2,2-propane.

Mainly used for epoxide
resins.

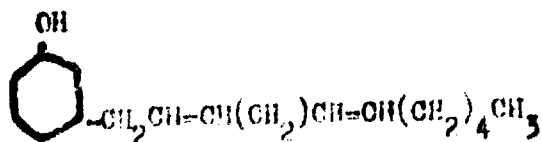
DIAGRAM 19

OABHEW-NUT-FIBER-LIQUID.



by solvent
extractions

Loses CO₂ on
 heating, i.e.
 during processing
 to extract the kernel.



Cardanol.

~~-2,8-~~ pentadecadienylphenol.

Possesses mixed functionality i.e. undergoes reaction with aldehydes,
 can polymerize via the unsaturated groups or by etherification between
 the phenolic hydroxyl groups and the unsaturated groups. The polymers
 are also reactive with aldehydes to give cured products.

Cured polymer - ground to friction dust for brake linings.

Polymers used in chemically and oil resistant cements and sealing compositions.

Cardanol can be distilled off (Vacuum or superheated steam) and used as a modifier for other phenols to produce a range of binder resins and rubber modifying resins.

DIAGRAM 22

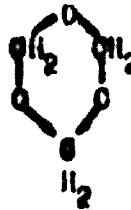
ALDEHYDE VARIANTS.

- **General Purpose:** - Formaldehyde H_2CHO Boiling Point $-19.2^{\circ}C$.

Normally obtained as a 37% by weight solution in water - Formalin
 But solutions of up to 50% may be obtained commercially.

Liquid formaldehyde polymerizes spontaneously to low molecular weight products, which are used commercially as sources of formaldehyde. Most important are:

Trioxymethylene



Paraform

$HO.(CH_2O)_n.H$ Where n can vary from 9 to 100

Acetaldehyde:



Used only infrequently.

Butyraldehyde:



It parts improved chemical resistance compared with formaldehyde, coupled with slight flexibility and improved compatibility with drying oils and rubbers. Gives resins of dark colour

Ammonium hydroxide - when used in conjunction with low aldehyde ratios low melting solid resoles may be obtained, having reduced solubility in water but good solubility in lower alcohols. The electrical properties of these resins are superior to those catalysed with sodium hydroxide.

Triethanolamine - Frequently used to formulate resins having high water dispersability.

Barium hydroxide - Subsequently neutralised with sulphuric acid and removed as barium sulphate is used to produce salt-free, resins of low ash content.

2. Novolaks

When conventional acid catalysts are employed, such as oxalic acid or sulphuric acid, the resulting novolak chains contain methylene linkages substituted in both the ortho and para positions on the phenol nuclei. Various techniques have been discovered whereby the proportion of ortho-ortho linkages is maximised. The most important of these is the use of Group IIb metal salt catalysts, such as zinc acetate. The importance of the *High Ortho* novolaks lies in their faster cure coupled with superior flow characteristics.

While resoles are mainly employed in aqueous or alcoholic solution or as syrups of up to about 85% solids content for a very wide variety of industrial applications, the main applications of the novolaks include:

Moulding Powders: The crushed novolak, together with hexamine, reinforcing filler (mostly woodflour) pigments, lubricants are compounded either on heated

rolls or in a heated extruder-mixer carefully controlled to specific curing times and flow characteristics, rapidly cooled and granulated to specific screen sizes. Such powders, which may be pre-formed as large pellets, are fabricated by compression or transfer moulding. In recent years injection moulding techniques have also been developed.

Powder Resins: Novolaks may be ground to mesh sizes as fine as 200 mesh and blended with suitably ground hexamine. Such combinations form the basis of many dry forming operations including abrasive wheels, clutch linings disc and moulded brake linings.

Solutions: Solutions of novolaks in lower alcohols are used in the pre-coating of sand for the production of shell moulds and cores for foundry use and in the manufacture of flame cureable sprays for coating foundry moulds.

AMINOPLAST RESINS

Of the aminoplasts the urea-formaldehyde resins are of considerable importance as they represent the cheapest of the thermosetting binders. They are almost invariably employed when product cost is the overriding factor. Their most important outlet is for general purpose wood bonding ranging from plywood to chipboard manufacture. The manufacture of low-priced pastel shade moulding powders. U-Fs may be foamed during the curing operation usually by mechanical whipping. In this form they are used in the preparation of thermal insulation within cavity walls, as foam blocks for flower display (*Florapak*) and, when the pores are filled with paraffin, as fire-lighters. In contrast to the phenolics which tend to be brown in colour and have a tendency to yellow with age, the aminoplasts are translucent white in colour. Unfortunately, the U-Fs suffer from

the disadvantage of poor water resistance and durability. When these conditions are demanded, the phenolics are usually employed. When high water resistance and durability, coupled with pale colour, is demanded, melamine-formaldehyde resins are used. Typical examples of such applications are the use of moulding powders based upon melamine-formaldehyde resins in the manufacture of plastic tableware and the use of melamine-formaldehyde resins in the surface papers of decorative laminates.

Other, perhaps lesser known, applications for aminoplast resins include:

Textile Sizes and Dressings - particularly to impart crease resistance in drip-dry apparel.

Wet-Strength Papers: Urea-formaldehyde and more frequently melamine-formaldehyde resins are added at the beater stage of paper formation to impart high wet strength in items ranging from bank notes to packaging and filter papers.

Fertilisers: Curcd U-F resins have been used as slow release fertilisers as a nitrogen source for lawns etc.

In general the initial condensation products of aminoplasts have a higher water solubility than those of the phenolics. On further condensation they form colloidal dispersions and gels which are capable of undergoing syneresis. Their solubility in alcoholic solvents may be enhanced by combining the methylol compounds with lower alcohol, particularly methanol to give improved stability in methanol-water solutions and with butanol to impart partial solubility in hydrocarbons. The butylated melamine formaldehyde resins, plasticised with non-drying oil alkyds, particularly from castor oil, form the basis of the stoving finishes employed in the manufacture of such consumer durables as refrigerators.

The main aminoplasts are outlined in Diagram 21. The chemistry of resin formation is rather more complex than that of the phenolics, certain aspects of it being still rather speculative.

Although the initial methylation reaction is effected under mildly alkaline conditions, with further condensation being heat induced, final cure may be catalysed by the presence of acidic materials, including phosphoric acid for foams, ammonium chloride for wood bonding or latent hardeners for moulding powders.

Combinations of aminoplast resins with cellulose have remained important since their commercial inception during the early 1920's. Cellulose remains the most important filler for aminoplast moulding powders and at the cruder end of the scale U-F resins are still used extensively as the binders for pulp mouldings, typified by egg boxes.

EPOXIDE RESINS

Although epoxide resins may be prepared from a variety of dihydric phenols, phenolic novolaks and the like, in practice the commercial resins are mainly based upon the reaction of epichlorhydrin with bisphenol A. The typical reactions being shown in Diagram 22. They are characterised by a unique range of properties having a combination of chemical resistance, adhesive character and relative lack of brittleness and low shrinkage during cure.

The molecular weight of the resin, in the uncured state, is entirely controlled by the proportions of reactants selected. As their cure is dependent largely upon the reaction of the terminal epoxide groups they are generally not as highly cross-linked as many of the other thermosets, hence their capacity to accommodate a higher degree of internal stressing.

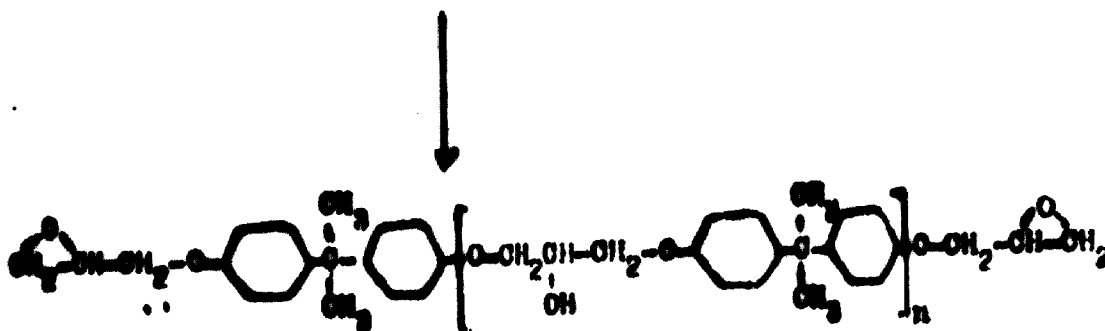
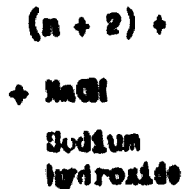
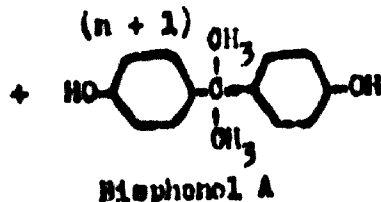
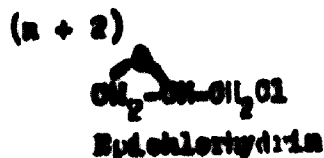
Unlike the phenolics and aminoplasts, they are not capable of cure by heat alone, but require the action of hardening agents or catalysts.

Principal hardening agents include acid anhydrides, phenolic and aminoplast resins, in the latter case, particularly, butylated melamine resins. These particular combinations are all characterised by the need for heat during the curing operation.

The two types of catalyst systems by which epoxide resins can be cured under ambient conditions include tertiary amines and Lewis acids, such as boron trifluoride, both of which contain a lone pair of electrons on the central atom which is capable of initiating polymerization by rupturing the epoxide ring.

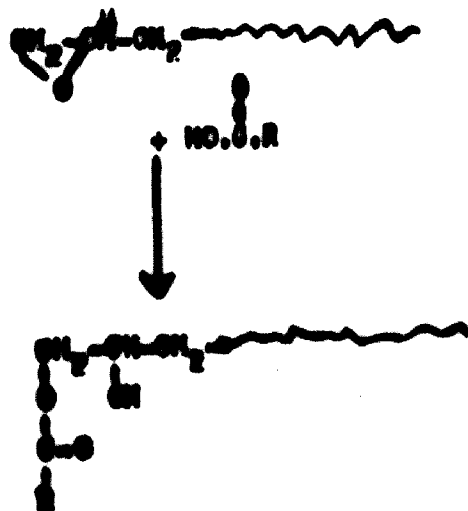
DIAGRAM 22.

EPICHLORHYDRIN RESINE.



<u>Sample</u>	<u>Resin state</u>	<u>Application</u>
0	liquid.	} Coating, adhesives, reinforced plastics frequently cold-cured using aliphatic di and poly amines.
0.6	do.	
1.0	Solid- M.Pt 65°0.	} Hot curing systems with aromatic diamines; di- acid anhydride and other aldehyde resins as curing agents. Also reactive with drying oils. - see below
16.0	Solid-MPt. 150°0.	

Reaction with Drying Oil Fatty Acids - Epoxy ester!



where R is a fatty acid residue such as linoleic.

Epoxy ester - mainly used in surface coatings.

Important applications of the epoxide resins include:

Reinforced plastics - by virtue of their adhesive capacity the resin-glass fibre bond is of high strength and the inherent chemical resistance of the cured resin is exploited in the manufacture of such items as tanks for the chemical industry.

Castings - The combination of low shrinkage, excellent adhesion and clarity make the epoxides eminently suitable for the encapsulation of electrical and electronic components. Larger casting of epoxides filled with inert mineral fillers have gained a considerable hold in the manufacture of patterns, jigs and stretch tools, while their chemical resistance has enabled epoxy castings to be utilised in the manufacture of pipes, joints elbows and pump casings for the chemical industry.

Adhesives - The use of epoxides in adhesives ranges from domestic two-part cold curing adhesives sold in squeeze tubes - the only really satisfactory type of adhesive for repairing broken china - through to structural adhesives for the aircraft industry.

Epoxy Esters, which have been developed as surface coating media, are normally prepared by reacting drying oil fatty acids with solid epoxide resins. In this reaction, both the hydroxyl groups and epoxide groups of the resin are functional.

UNSATURATED POLYESTER RESINS

Unsaturated polyester resins are essentially solutions of mixed glycol maleate/phthalates dissolved in a vinyl monomer with which they co-polymerize during the curing process to give clear, pale coloured infusible-insoluble products. By far their main application is in the manufacture of reinforced

plastics. It was, in fact, the development of the unsaturated polyester system which enabled the reinforced plastics field to develop to the extent which it has today.

A typical general purpose resin, the preparation of which is outlined in Diagram 23, would consist of a 60% solution of an ethylene glycol maleate/phthalate, having an approximate phthalic anhydride to maleic anhydride ratio of 2½ to 1, in monomeric styrene. Special purpose resins being derived from such a product by combinations of variation in the proportions of the ingredients and substitution of alternative ingredients, the most important of which include:

<u>Variant</u>	<u>Effect</u>
Increase in maleic content	Improved reactivity, thermal stability, rigidity and resistance to chemicals and weathering.
Use of propylene glycol in place of ethylene glycol.	Improved styrene tolerance i.e. lower viscosity solids ratio.
Use of isophthalic acid in place of phthalic anhydride.	Improved flexural strength and moduli, lower water absorption.
Partial or complete replacement of phthalic anhydride by tetrachlorophthalic anhydride or chlorendic acid.*	Fire resistance.
Partial replacement of styrene by methyl methacrylate.	Improved transparency of glass fibre composites.
Replacement of styrene by diallyl phthalate.	Non-volatile monomer - used in pre-impregnation processes.
Addition of U-V stabilisers.	Reduction of after-yellowing.
Addition of colloidal silica.	Imparts thixotropy.

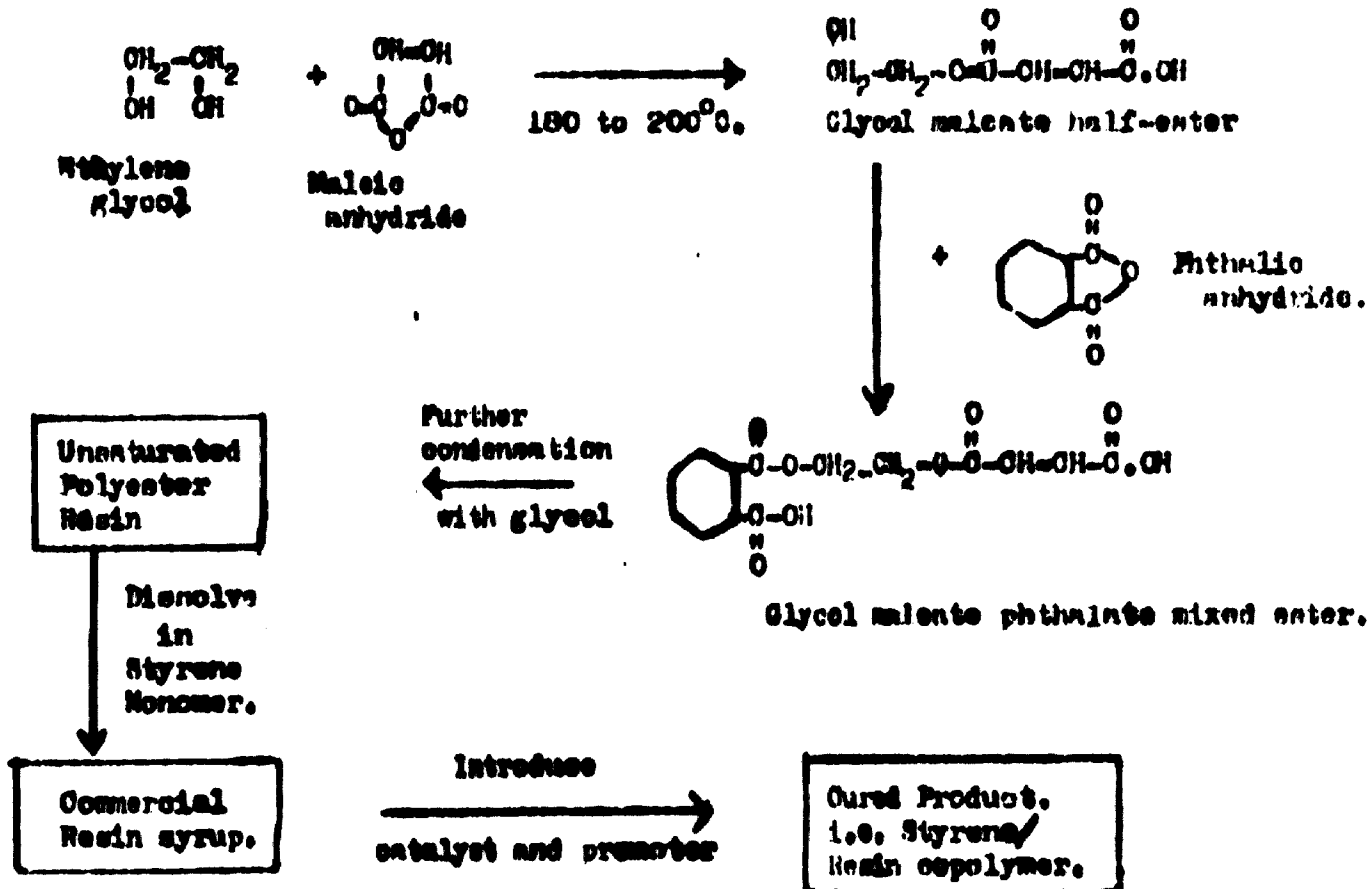
* Chlorendic acid - the adduct of hexachlorocyclopentadiene and maleic anhydride.

Premature gelation during transit and storage is prevented by the incorporation of inhibitors, particularly, hydroquinone.

DIAGRAM 23.

UNSATURATED POLYESTER RESINS

Resin Preparation - Half Ester Process.



Catalyst - Promoter Systems

<u>Catalyst</u>	<u>Promoter</u>	<u>Cure</u>	<u>Remarks</u>
1. Benzoyl Peroxide	Dimethyl aniline	Cold	Poor colour
2. Benzoyl Peroxide	Nil	Hot	Used for matched die moulding.
3. Methyl ethyl ketone Peroxide	Cobalt naphthenate	Cold	Most popular for hand lay-up etc.
4. Cyclohexanone Peroxide	Cobalt naphthenate	Cold	Faster than 3 but more expensive.
5. Cyclohexanone Peroxide	Vanadium naphthenate	Cold	Best colour (i.e. polyst)

The resins may be cured by the addition of combinations of peroxide catalysts and promoters either at ambient temperatures or by heating. The curing process invariably involving an exothermic reaction. Typical catalyst-promoter combinations being shown in Diagram 23.

The proportions of catalyst and promoter can be adjusted to give a wide range of curing rates and normally are varied between 0.5 and 2.0% of the resin.

OIL MODIFIED ALKYDS

By far the most important range of resins used in the preparation of paints, varnishes and lacquers are the oil modified alkyds, the world production of which is in excess of 1 billion tons per annum. Modified alkyd generally are described (see Diagram 24) as linear polyesters containing pendant fatty acid groups. This description is an oversimplification of the most important group, the drying oil modified alkyds as during manufacture, polymerization, adduct formation and other side reactions lead to a much more complex situation.

Alkyds are classified according to the following factors relating to their composition:

1. Type of Oil modification - Whether drying or non-drying oil fatty acids are used.
2. Proportion of Oil used - 'OIL LENGTH'

<u>Oil Length</u>	<u>Oil Content</u>	<u>Phthalic Anhydride Content %</u>
Short	35-45	above 35
Medium	46-55	30-35
Long	56-70	20-30
Very Long	Above 71	below 20

3. Polyhydric alcohol employed - A fairly wide range of polyols may be used the most popular being glycerol and pentaerythritol, less common polyols include, for example, dipentaerythritol and trimethylolethane.

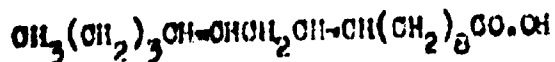
DIAGRAM 24

OIL MODIFIED ALKYDS

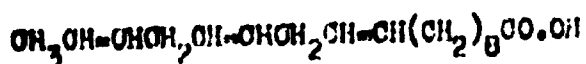
Phthalic esters of polyols modified by drying oil fatty acids.

Drying Oils Comprise mixed glycerides of long chain (C₁₈), polyunsaturated fatty acids. The main drying oils containing:

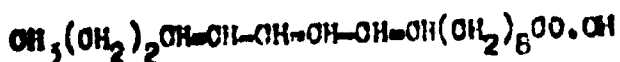
Linseed Oil - I. Linoleic acid - 9,12-octadecadienoic acid.



II. Linolenic acid - 9,12,15-octadecatrienoic acid.



Tung Oil - Eleostearic acid - 9,11,13-octadecatrienoic acid.

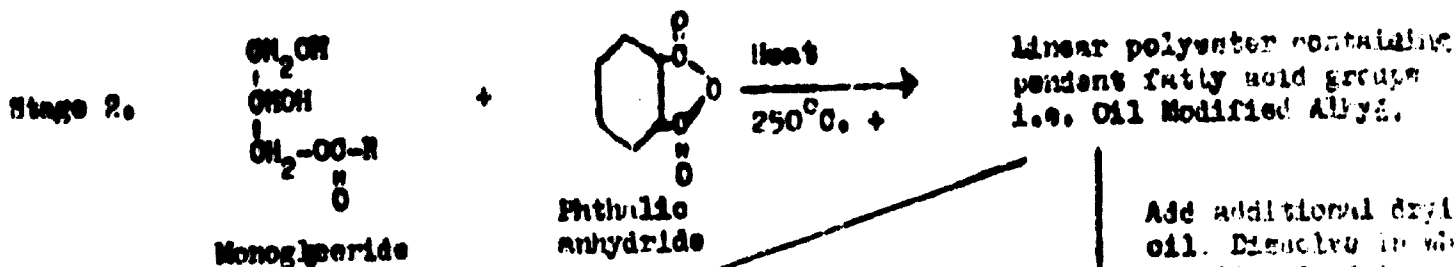
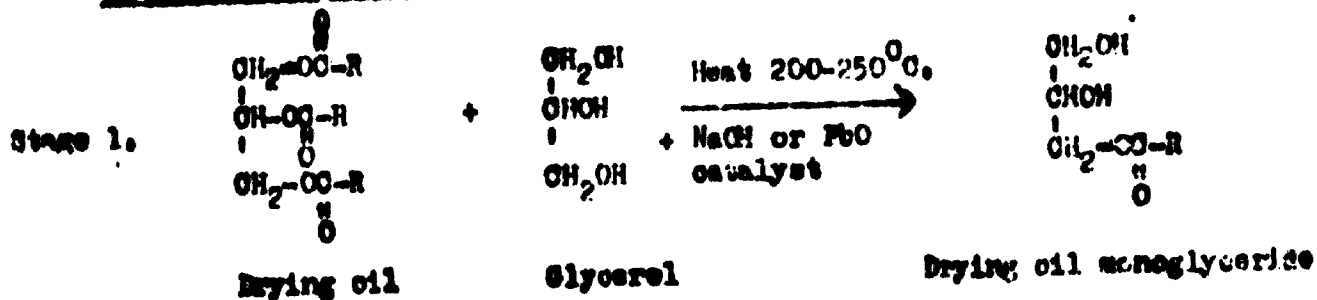


Castor Oil - Ricinoleic Acid - 12 hydroxy-9-octadecenoic acid (Non-drying)



Which dehydrates on heating in the presence of catalysts to Dehydrated Castor Oil containing Linoleic acid.

ALKYD MANUFACTURE - Ester Interchange Process



Further Modification
e.g. Styrenation

↓
Add additional drying oil. Dissolve in methyl spirit, add driers
↓
Air drying varnish medium for paints

4. The dibasic acid employed - Although phthalic anhydride is by far the most commonly employed, isophthalic acid has gained in popularity, and the more flexible aliphatic diacids such as adipic and sebacic are used for special purpose formulations. Unsaturated acids, particularly maleic anhydride and fumaric acid may also be employed as replacements of partial replacements for the phthalic anhydride.
5. The precise fatty acid and/or oil used - Among the drying oils the following, roughly classified according to their reactivity, are:

<u>Oil</u>	<u>Iodine value (Unsaturation)</u>	<u>Drying Speed</u>
Tung	170	Fastest ↑ Slowest
Linseed	180	
Dehydrated castor	155	
Safflower	140	
Soya	135	
Tall oil (fatty acids)	125	
Castor	85	
Coconut	9	(Non-drying mainly used for plasticising butylated aminoplast stoving finishes

The manufacturing process outline described in Diagram 24 is the most popular of a number of so-called fusion processes. During recent years, however, it has been found that better control may be exercised during the esterification stage by the addition of entrainers, particularly aromatic hydrocarbons to effect azeotropic removal of the water of condensation. Very many further modifications of alkyds are possible. These may be based upon blending with other products such as resin based materials, phenolic, aminoplast epoxy and silicone resins or the chemical modifications involving, for example, styrenation or malienization.

POLYURETHANES

The common reactions capable of being undergone by isocyanate groups, which are described in Diagram 25, indicate some idea of the scope arising in the preparation of polyurethane, polyureas and polyallophanates, which provide the basis of polyurethane chemistry.

In view of the complexity of the reactions involved and the variety of possibilities, it is convenient to classify the polyurethanes by their end-use applications in the broad terms of:

Elastomers

Castings of varying degrees of flexibility and hardness

Adhesives

Surface coatings

Rigid and flexible foams

which can be illustrated by the following selected examples.

Elastomers:

Polyurethane rubbers, possessing a high order of chemical resistance, abrasion resistance and durability can be prepared by the reaction of long chain diols, polyester or polyether based, with excess diisocyanate, frequently diphenylmethane diisocyanate to produce isocyanate terminated chains which are then extended by reaction with glycols, diamines or triols. During the chain extension reaction, for example with glycols, some interaction between the urethane groups formed and other terminal isocyanate groups, occurs to initiate cross-linking via allophanate groups.

Coatings:

Tough, chemical and abrasion resistant coatings based upon polyurethanes may be classified as two part, one shot or polyurethane oils.

The two part coatings comprising for example, a triol reacted with excess diisocyanate to give isocyanate termination as one component which then cures on mixing with a hydroxy terminated polyester or polyether.

DIAPAM 25

POLYURETHANES.

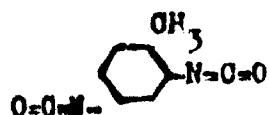
Derived from the reaction of diisocyanates with di or poly:

Hydroxyl compounds, including water.

Carboxylic compounds.

Amino compounds

The principal diisocyanate used is a mixture of isomers of toluene diisocyanate rich in the 2,4- and 2,6- isomers. (TDI)



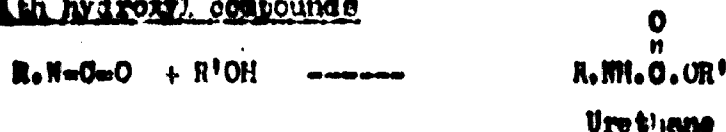
2,4-toluene diisocyanate



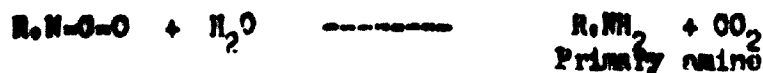
Urethane group.

Typical reactions of the isocyanate group includes:

1. With hydroxyl compounds



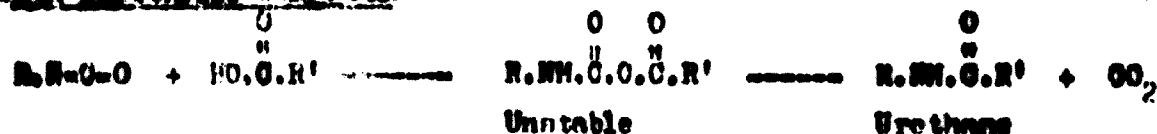
2. With water



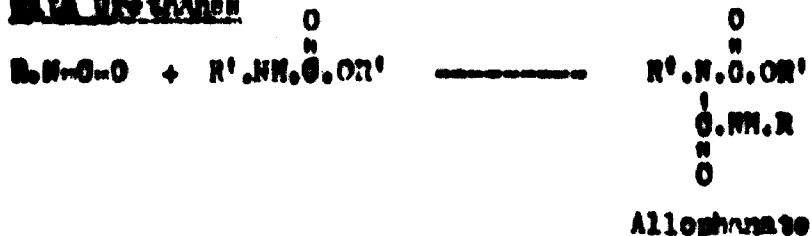
3. With Amine



4. With carboxylic compounds



5. With Urethanes



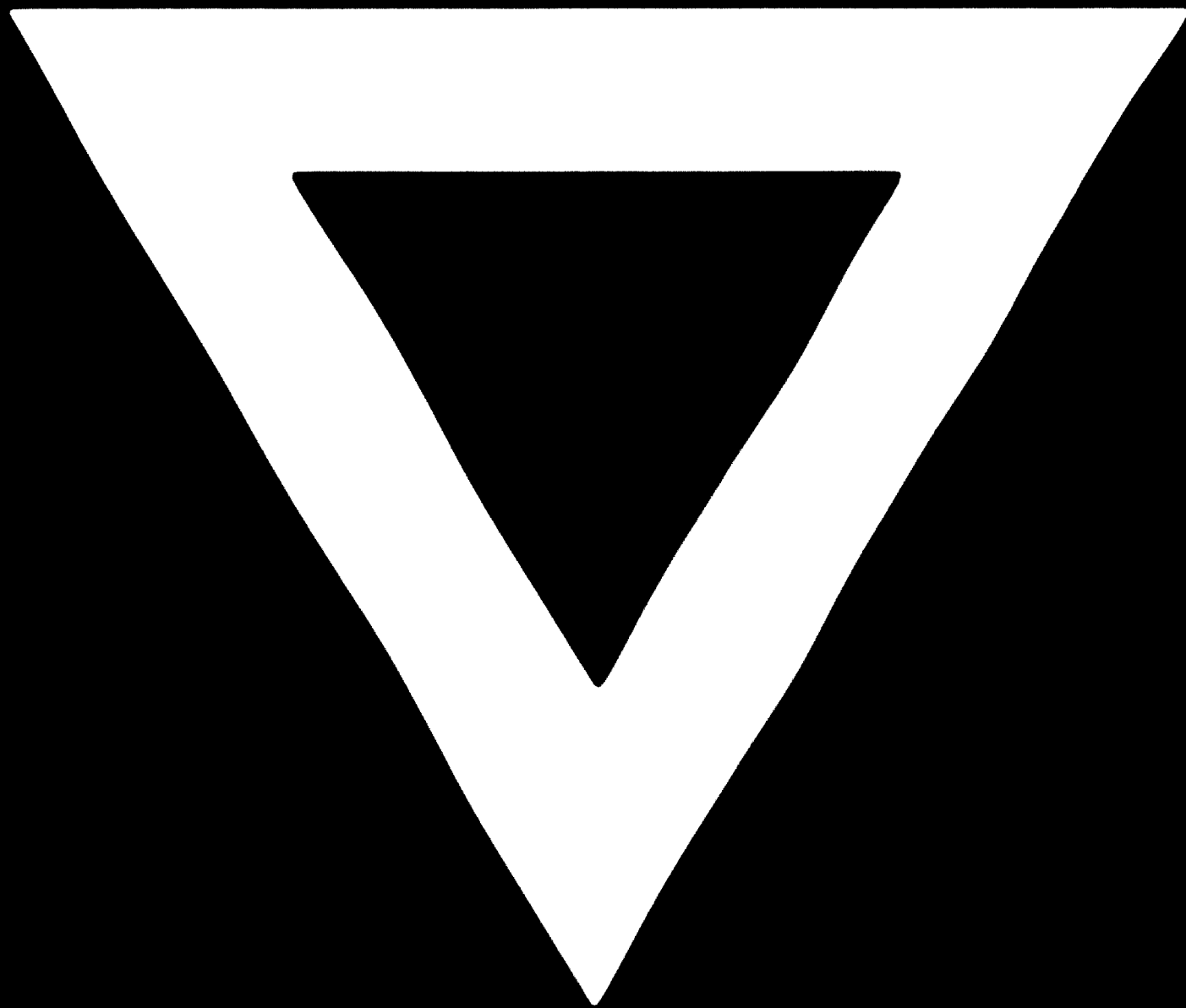
The one shot system is based upon a stable isocyanate terminated pre-polymer which cures by reaction with atmospheric moisture. The urethane oils are based upon isocyanate modified drying oils. The oil is alcoholised with glycerol to a mixture of mono and diglycerides which are reacted with diisocyanate to increase their molecular weight, final drying being effected by normal oxidative polymerization.

Foams :

Originally flexible polyurethane foams were prepared by reacting carboxy terminated polyesters, such as polyethylene glycol adipate, with toluene diisocyanate which simultaneously effected cure and liberated carbon dioxide. More recently, polyethers have become popular as starting materials, in addition to being hydroxy terminated, they also contain hydroxyl groups pendent to the molecular chains. Cure and foaming being brought about by the introduction of toluene diisocyanate and water, in conjunction with a tertiary amine catalyst to accelerate the urethane reaction. To produce rigid polyether foams the proportion of non-terminal hydroxyl groups is increased to effect a higher degree of cross-linking and the introduction of higher proportions of aromatic nuclei.



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