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UNIDO-project

CONTRACT N° 83 - 34

PROJECT N° UF/GLO/81/059

15517

DEVELOPMENT
OF
LIQUID NATURAL RUBBER

FINAL REPORT

777

INSTITUT DE RECHERCHES SUR LE CAOUTCHOUC

IRCA - CIRAD

CONTRACT N° 83 - 34

UNIDO PROJECT N° UF/GLO/81/059

JANUARY 1984 - DECEMBER 1985

DEVELOPMENT
OF
LIQUID NATURAL RUBBER

FINAL REPORT

REPUBLIQUE DE COTE D'IVOIRE

**MINISTERE DE L'EDUCATION NATIONALE ET
DE LA RECHERCHE SCIENTIFIQUE**

INSTITUT DE RECHERCHES SUR LE CAOUTCHOUC

IRCA

Département du Centre de Coopération Internationale en
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SUMMARY

Contents — Page

CHAPTER - 1

INTRODUCTION AND PRELIMINARIES

1.1. INTRODUCTION

Liquid rubber has been defined by Eric Sheard in his 1972 and 1981 reviews as an elastomer or elastomer precursor which can be poured or pumped (with a viscosity below 1500 poises) at temperatures up to 100° C before undergoing some type of cure ; either chain extension, crosslinking or both. Since liquid rubbers are pumpable it is possible to cast them into a variety of intricate shapes and cure "in place", and since they contain no water or volatile solvents there is little or no shrinkage following curing. Natural and synthetic rubbers are also available as suspensions in water or dissolved in a variety of solvents. It is difficult to derive a satisfactory definition that distinguishes between the liquid rubbers and these rubber latices and solutions since it is possible to manufacture cast products using these materials. In order to distinguish between liquid rubbers and the rubber latices and solutions, Sheard's definition of liquid rubbers should be modified to become ; liquid rubbers are elastomers or elastomer precussors that can be poured or pumped at temperatures below 100° C without the assistance of an external medium.

The concept of a pumpable and castable LNR has been of considerable interest for a long time to processors and manufacturers of NR goods. A LNR would enable these manufacturers to take advantage of the manufacturing processes already available to manufacturers employing synthetic liquid rubbers and resins or the powder technology employed by plastics manufacturers and processors. These advantages would include the use of automated metering equipment, lower processing energy requirements, lighter equipment and shorter cycle times. The use of liquid rubber also offers the possibility of using in-place cures following casting into more intricate and larger shapes.

Since the 1920's there have been considerable developments in the field of liquid rubbers. The first LNR became commercially available in the USA in 1923. Only 2 years later a liquid polybutadiene, Plastikator 32, manufactured by a German firm. Between this time and the 1940's, considerable work was done on the development of peptizers. From this work a process was developed in the UK for manufacturing LNR by the chemical depolymerization of rubber in solution using cobalt linoleate. This LNR was called "Rubbone" and though production trials were undertaken this process was never commercialised. It was not until the early 1950's that a commercial process for LNR manufacture was established in the UK. It took until 1943, however, for liquid synthetic elastomers to became an important sector of the elastomers market with the development at Thiokol of liquid polysulphides. It was first used as a self-sealer for aircraft fuel tanks but since then it has been used in a wide variety of applications, including sealants, moulds, for cable filling, and as a binder. Its development as a binder for rocket propellants created considerable demand for liquid elastomers with reactive terminals that would produce a three-dimensional network when cured and give the necessary dimensional stability to the rocket fuel. Liquid elastomers with reactive terminals have been defined as the second generation liquid rubbers.

In 1972, RAPRA defined liquid rubbers as :

1st generation	- no reactive terminals leading to low physical properties,
2nd generation	- reactive terminals, low physical properties, eg functional polybutadienes,
3rd generation	- low MW, reactive terminals, good physical properties eg liquid silicones and polyurethanes.

The first generation liquid rubbers, including LNR and nonfunctional polybutadienes without reactive terminal groups, cannot be chain-extended to recreate the rubbery properties of the original elastomer. These elastomers do have specific applications ; for example butyl is used in mastics and sealants because of its excellent ageing properties. The market for liquid elastomers expanded with the introduction of the more versatile second generation liquid rubbers but the dramatic increase in this market came with the arrival of the third generation liquid rubbers, the polyurethanes and liquid silicones, which have been available for the last 10 years. They now dominate the market for liquid rubbers for, despite their high cost, they can be tailored chemically for almost any application.

UNIDO and IRRDB project of development of liquid natural rubber :

Following a symposium held in May 1981 in Phuket, Thailand, on the new forms of natural rubber, UNIDO granted IRRDB a special contribution of US $ 1,200,000 paid by the Federal German Republic to transpose on a semi-industrial stage (200 kg per operation) in a natural rubber producing country, the Ivory Coast, the process developed by IRCA and IRAP. The existing qualities of low molecular weight polysoprene were so far made either by polymerization of the isoprene monomeride or by mechano-chemical depolymerization of compact natural rubber.

The aims of the project, defined in "Terms of reference dated 28th December 1982" were :

- to select the most promising routes to the preparation of liquid NR,
- to assess the industrial applicability of liquid NR in terms of properties and economics,
- to develop liquid NR to a stage where its production in NR producing countries can be carried out.

This new technique will reinforce the competitiveness of natural rubber towards its synthetic competitors and, by widening its possible uses, will give natural rubber producing countries, the Institutes of which are IRRDB members, new assets to increase natural rubber development.

1.2. PRELIMINARIES

1.2.1. Depolymerization process adjustment to field latex

A patent registered by the Institut Français du Caoutchouc described the depolymerization process from rediluted or non-rediluted centrifuged latex. It therefore was important to check whether the process could be applied to field latex which contains a larger amount of non-rubber elements and whose colloidal structure, especially the size of rubber particles, is very different.

Tests conducted on field latex have shown that the process could perfectly be used. The parameters of the depolymerization reaction could thus be optimized for the running of the pilot plant built in the Côte d'Ivoire. They are the following :

- latex DRC 30 %

- latex stabilization by 0.2 % NaOH and 1 % ammonia soap ([illegible])

- 9 % phenylhydrazine in weight of dry rubber to obtain a viscosimetric molecular weight, Mv from 9 to 11,000 ; a higher percentage of phenylhydrazine gives a LNR with a Mv of 7,000 ; by reducing the percentage of phenylhydrazine, it is easy to obtain Mv ranging from 20 to 30,000

- air flow : 60-80 l/mn per 200 kg of dry rubber

- reaction temperature : 65° C

- reaction duration :24 continuous hours

- coagulation by acetic (50 g per kg of dry LNR) or formic (40 g per kg of dry LNR) acid

- washing

- vacuum drying at 60° C.

A method for quickly determining the depolymerization state has been finalized and successfully developed.

Studies on the noxiousness of effluents have shown that they could be discharged in lagoon waters after decantation, neutralization and filtration.

Allergy tests with LNR have been negative.

1.2.2. Commissioning tests

These took place in October 1984, in the factory that produced the pilot plant, in the presence of UNIDO and UTA representatives, with the following objectives :

- check the smooth running of the pilot before its shipping

- check the good adaptation to field latex of the depolymerization reaction parameters.

1.2.3. Setting up of the pilot plant in the Côte d'Ivoire

Civil engineering works have been conducted in the Côte d'Ivoire from April to October 1984, to construct a building meeting the specifications laid down by the pilot manufacturer :

- length : 18 m
- width : 9 m
- height : 6.5 m.

Having been dismantled, the pilot plant arrived on the site in January 1985, reassembled and started up early April 1985.

Reception tests gave rise to an official inaugural ceremony to which participated representatives of the Government of the Côte d'Ivoire, of UNIDO, GFR and IRRDB.

The starting up did not raise any difficulty.

1.2.4. Production of LNR in the Côte d'Ivoire

The pilot plant has run perfectly, at the rate expected of one reaction a week, i.e. 200 kg dry liquid rubber per operation. It made it possible to produce LNR with various molecular weights ranging from 7,000 to 25,000. It also allowed to produce depolymerized latex coagulum for the development of a continuous flow dryer and to meet all the sampling requirements.

While this pilot plant was running, a new phenomenon of depolymerization appeared during coagulation. It could not be emphasized in the laboratory. It has been controlled modifying some operating conditions (cold rapid coagulation). The pilot plant has therefore perfectly reached the first objective, which was to pass from the laboratory to the industrial stage.

A small laboratory pilot has been set up to carry out various accompaniment studies including :

- search for a system of field latex stabilization,

- attempted study of the clonal effect,

- study of coagulation conditions.

1.2.5. Chemical modification of LNR

Chlorine modification :

Liquid rubber is dissolved in carbon tetrachloride at a concentration of 8 %.Chlorination occurs at atmospheric pressure by chlorine bubbling under ultraviolet rays. Chlorinated rubber is recovered after carbon tetrachloride is removed by a stripping. The product obtained is perfectly suited to manufacture anticorrosive paints and some adhesives.

Maleic anhydrid modification :

Two possible mechanisms of maleic anhydrid fixation on LNR have been studied.

The first is of radical type : it is induced by moderate temperature heating in presence of free radical catalysers.

The second is of thermal type : it is induced by high temperature heating without any catalyser.

Finally the chemical modification by thermal way has been chosen because it is giving better fixation rates up to 65 % in simplified operating conditions.

For a modification rate about 20 %, the modified polymer possesses interesting adhesive properties which are comparable to those of certain structural adhesives ; however the use of a solvent may be an handicap.

The presence of reactive sites such as succiniques anhydrid cycles makes it possible to envisage the fixation of active substances giving access to products with a higher value added.

Epoxydation of latex of depolymerized natural rubber is achieved in conditions that are identical or even easier than those of latex of high molecular weight rubber. It leads to a wide range of products, some of which will find outlets especially in the adhesive industry.

Grafting of antioxydants :

An LNR/4 nitroso-diphenylamine adduct does show some promise as an antioxidant capable of becoming "network bound". In assessing the findings however, due account must be paid to two other considerations. First, experience both at MRPRA and elsewhere, has shown that in this area prediction of service performance from laboratory data is very uncertain. Second, and probably more important, the likely carcinogenic character of NDPA renders its commercial use, even as a precursor, subject to considerable constraints. Alternative chemical routes could doubtless be devised but these are most unlikely to be economically viable.

1.2.6. Industrial applications and development in the laboratory

Considering the predictable fields of LNR utilisation, formulae have been developed in the following sectors :

- LNR vulcanization and technological properties of vulcanization,
- LNR based compounds vulcanizing at moderate temperature for low hardness and pourable compounds and preparation of flexible moulds,
- LNR for cellular rubber,
- LNR as a reactive plasticizer and processing aid,
- LNR used as an abrasive particle binder for grinding wheels,
- LNR as a coating agent for pulverulent chemicals.

LNR development :

Contacts have been established in the above-mentioned application fields in France, GFR, Great Britain and the USA : tyres, industrial rubber, glues and adhesives, wires and cables, chemical products used in the rubber industry. As to the potential end-uses for the LNR one of the most promising is its use to coat rubber chemicals. This market could use in excess of 100 tons LNR/year. There is also a substantial market in Western Europe for LNR in the manufacture of grinding wheels. Up to 300 tons /year of liquid rubbers are consumed by this industry and a futher 300 tons of masticated natural rubber. This masticated rubber could be subsituted by LNR (as well as some of the liquid rubber) if manufacturers recieved assurances about continuity of supply and maintenance of quality control.

It is difficult to sustantiate other end-uses. Depolymerized NR is already sold for use in mastics and this market could be increased if the price of the LNR was competitive with other materials currently used; for example, a substantial market could be created if LNR was used to replace some of the more expensive polysulphide. LNR could also be used for cable filling, though its use would be restricted since it cannot be used where temperatures exceeded 60°C. Its use as an encapsulating agent is also resticted by this constraint except for low power components. The colour and low MW of LNR limits its use in adhesives but it could still be used in low cost domestic glues (where the absence of organic solvents and water are definite advantages) and as a viscosity modifier in hot melt adhesives. There is also a small market of 2 tons /year as a binder in the manufacture of paint brushes.

Two of the major tyre manufacturers have received LNR samples and though they all indicated the possibility of substantial demand if the applications under consideration were successful, they did not identify what these applications were. The first has indicated a potential demand for 25 tons LNR/year for one application whilst the second was considering an application requiring in excess of 100 tons /year. Kuraray sell 600-700 tons of liquid synthetic polyisoprene to the tyre industry in the Far East where it is used as a tackifier. The potential of LNR in the European and American tyre industries is unclear and at the present time should not be included in the estimate of the readily available market. One of the largest in the world producer of rubber chemical is interested by LNR for a patented application.

The immediately available market for LNR is about 500 tons . This market is fragmented and a considerable marketing effort would be required to realise this market. As well as technical support LNR purchasers will demand guarantees for continuity of supply and maintenance of quality control. Demand for the LNR could be stimulated by offering a broad product range; for example LNRs of different viscosities and chemically modified LNRs, as well as by reducing the price of LNR. To do this manufacturing costs have to be minimised; by finding a cheaper source of phenylhydrazine and low cost investment capital.

A techno-economist has studied the estimate of LNR price at the pilot and industrial levels. Considering the short time available since the pilot plant started up, these figures are only an approach to a real price.

On the basis of the pilot plant established at the IRCA Côte d'Ivoire and a hypothetical industrial plant (1300 tonnes/year) designed by the pilot plant manufacturers (De Diétrich Cie - Reischshoffen France) with ROI being 15% over 6 years and capacity utilisation dropped to 60% manufacturing cost including working capital become Fr. 26.423/tons for the low viscosity LNR and Fr. 23.099/tons for the "high viscosity" LNR.

1.2.7. Conclusion

Reading these preliminaries shows that the contract lasted long enough to demonstrate unambiguously the smooth running of the pilot plant. On the other hand, the aspect of development has been well started on but time lacked to get the most out of all the activities undertaken.

CHAPTER - 2

DEPOLYMERIZATION PROCESS ADJUSTMENT TO FIELD LATEX

2.1.PRESENTATION OF THE PROCESS

The reaction of natural polyisoprene depolymerization involves the action of an oxydo-reducing couple (oxygen-phenylhydrazine) which, under some conditions, generates a polymere chains oxidizing break.

The original polyisoprene molecular weight, of around 600,000,-1,000.000, is decreased to 8,000 - 20,000 to obtain oligomeres of a more or less fluid consistency according to the conditions selected. The simplified reaction mechanism is illustrated by figure 2.1.

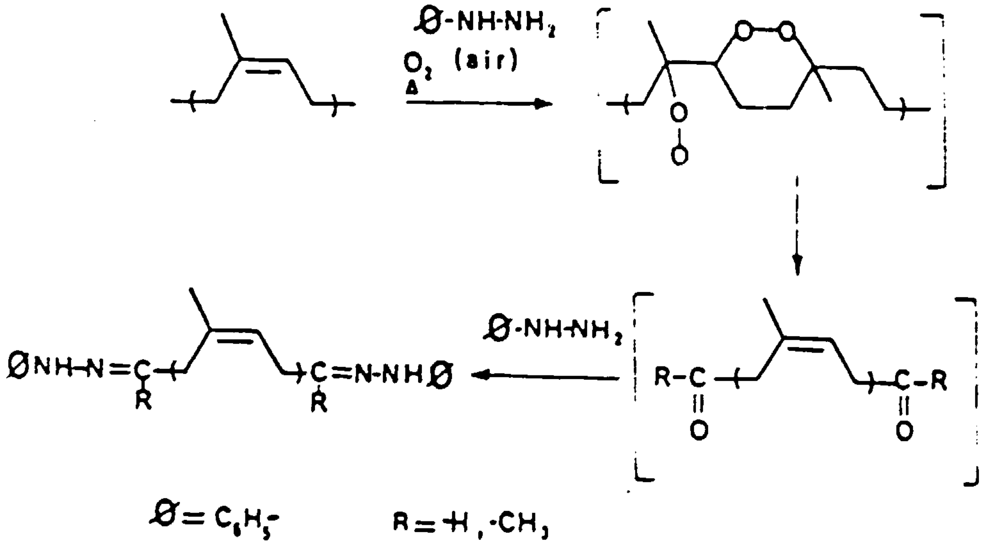


Figure 2.1

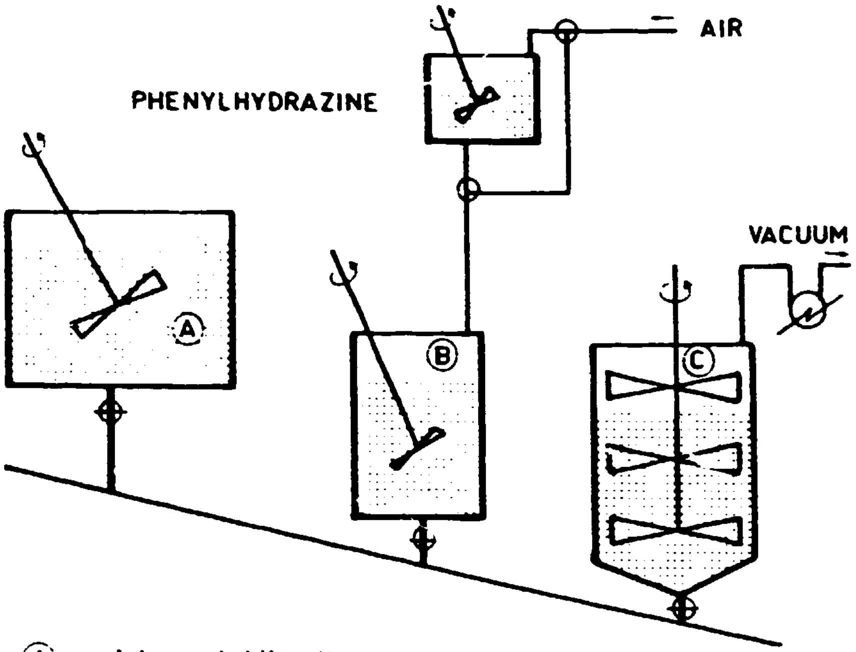
Depolymerization mechanism of 1,4 cis polyisoprene

The reaction process follows these stages (figure 2.2.) :

- latex stabilization and ammonia elimination (reactor A)

- depolymerization : addition of phenylhydrazine in a hot aqueous medium and air bubbling (reactor B)

- precipitation - washings - vacuum drying (reactor C)



Ⓐ = latex stabilization.

Ⓑ = latex depolymerization.

Ⓒ = latex coagulation-washing & drying of liquid rubber.

Figure 2.2.
Schematic layout of a natural rubber depolymerization unit

In the initial process, polyisoprene depolymerization had been studied on centrifuged latex. The initial DRC of 60 % was decreased to 50 % in presence of a stabilizing agent of the non ionic type (MERGITAL O) requiring the use of acetone in large quantities to precipitate liquid rubber.

The use of another stabilizing agent of the anionic type (NEKAL BX makes it possible to recover liquid rubber by coagulation thanks to a diluted acid such as formic acid.

At the same time, difficulties appeared in the small pilot unit existing in France with phenylhydrazine introduction.

According to introduction and agitation speeds, the formation of more or less voluminous coagula is observed, requiring the reactor be stopped to remove them.

The process has been improved : phenylhydrazine is added as solution emulsion in three times its volume of hot water, either by the air-intake pipe or directly. Addition can be much quicker, without producing any coagulum. Depolymerization kinetics is displayed on the graph of figure 2.3.

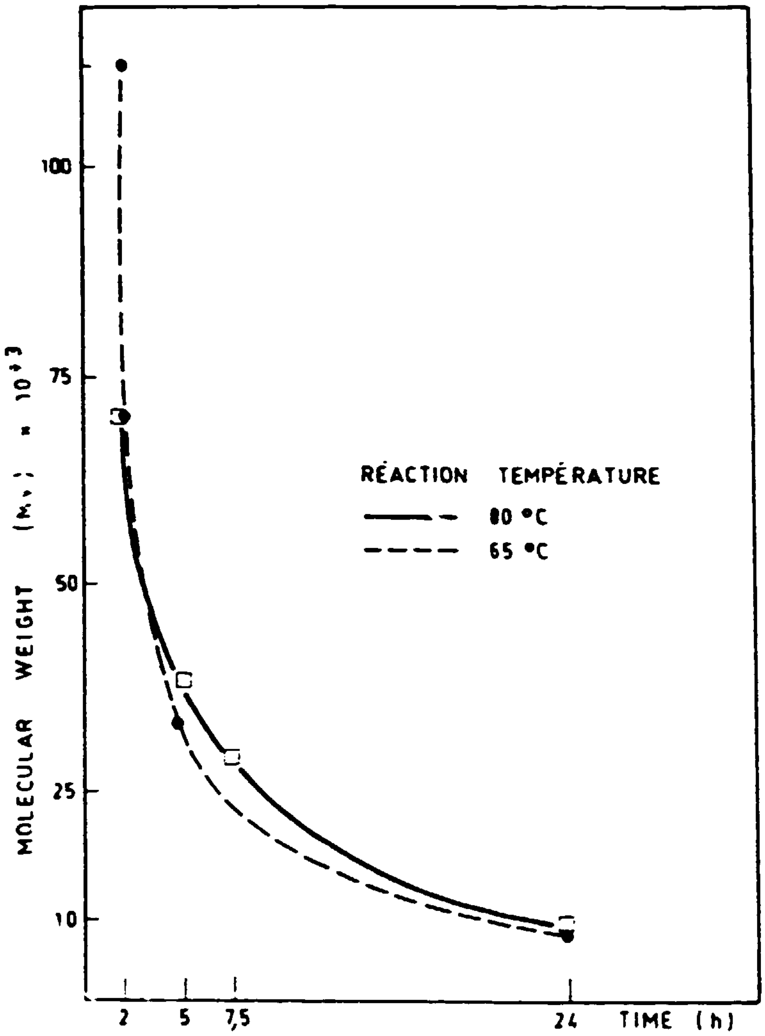


Figure 2.3.

Kinetics of depolymerization
- centrifuged latex
- $NH-NH_2$: 3.10^{-4} mole/g of rubber

Considering that field latex DRC * was near 30-35 % and that its composition differs from centrifuged latex (since the latter does not include a large part of non-rubber substances), this study aimed at, on the one hand, checking whether the conditions could to applied :

- to more diluted latex
- to field latex

and therefore transposed to the pilot unit established on the very production place, and, on the other hand, optimizing the conditions of reaction.

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* Dry Rubber Content

2.2. OPTIMIZATION OF THE CONDITIONS OF REACTION

Different deciding parameters have been particularly examined.

2.2.1. Conditions of phenylhydrazine introduction

In the laboratory, phenylhydrazine is introduced in the reactional medium in a few minutes. In the small pilot unit existing in France, introduction requires about ten minutes and this operation was sure to take longer in an industrial pilot unit.

It therefore seemed necessary to determine whether prolonged contact in hot water could partially decompose phenylhydrazine, impairing thus the effectiveness of the reaction.

The results of the tests L.1, L.2 and L.3, L.7, L.11 and L.17 carried out at 75°C and 65°C respectively, which are listed in table 2.1, show that phenylhydrazine reactivity is not affected by a one-hour stay in hot water.

On the other hand, one test showed that it was preferable that introduction should take place in the reactional medium brought to reaction temperature (test L.12).

2.2.2. Influence of reaction temperature

For the pilot plant,it was admitted in agreement with De Diétrich Company, that fluctuations of temperature of 5°C (± 2,5 °C) were possible. Experiments have been conducted covering the 35 to 85°C temperature range, 5 by 5°C.

According to the results of the tests L4 through L.10 (table 2.1), a large margin of safety has been determined, ranging from 45 to 75°C, without any modification in the molecular weight of the rubber produced.

To study the other parameters, the mean temperature of 65°C was adopted.

2.2.3. Latex concentration

A somewhat deficient reproductibility in the results had been observed for reactions performed under equivalent conditions but for which latex had higher concentrations (37 to 40% DRC).

In these cases, an increase in latex viscosity in the first instants of phenylhydrazine introduction had been observed in both the laboratory and small pilot unit existing in France. This phenomenon decreased the effectiveness of air-dispersion.

Control tests confirmed this hypothesis. Later on, a standard DRC of 30% was admitted.

Latex with higher initial concentration may be used in the small pilot unit, considering the power and effectiveness of agitation.

2.2.4. Combined influence of phenylhydrazine amount and air-flow

The main objective of this test series was mostly of an economic

Table 2.I

EFFECTS OF TEMPERATURE REACTION AND ADDITION CONDITIONS OF PHENYLHYDRAZINE ON DEPOLYMERIZATION REACTION (CENTRIFUGED LATEX)

Test number	L.1	L.2	L.3	L.4	L.5	L.6	L.7	L.8	L.9	L.10	L.11	L.12	L.13
Phenylhydrazine moles/g rubber x 10^{-4}	8	8	8	8	8	8	8	8	8	8	8	8	8
Reaction temperature	75	75	75	80	75	70	65	55	45	35	65	65	65
Stabilizer % pHR	1,5	1,5	1,5	1,5	1	1,5	1	1	1	1	1	1	1
Air flow (l/mn)	2,5	2,5	2,5	2,5	2,5	2,5	2,5	2,5	2,5	2,5	2.5	2.5	2.5
Conditions of phenylhydrazine addition	1 time	2 times (30 mn)	5 times (60 mn)	← 3 times →							Hot water 65 °C +stirring (30 mn)	1 time in latex at room temperature	2 times the second after 8,5 hours
Molecular weight ($\overline{M}v$)	12,500	9,700	11,200	13,400	8,800	9,700	7,500	9,300	8,100	13.800	8.900	11.900	8.400

nature. To obtain rubber of a molecular weight $\overline{Mv}$ near 10,000, it is necessary to use 10 phr (per hundred rubber) phenlyhydrazine.

Owing to the price of this reagent, trials to reduce the amount required to obtain the same result were important.

An experiment scheme has been devised, involving simultaneously :

- the amount of phenylhydrazine (4-6-8-10-12.10^{-4} mole/g of rubber)
- air-flow (1.5-2.5-4.5 l/mn in the laboratory; 5-7 an 10 l/mn in the small pilot unit).

The results appear in table 2.II.Despite the anomalies probably due to a defective air dispersion under the conditions of these tests, it can be concluded that, in both the laboratory and pilot unit, the air flows studied have no appreciable incidence on the polymerization state of the rubber obtained.

Anyway, it should be noted that this is a situation where oxygen is largely excessive. The result of this is that depolymerization effectiveness mainly depends on phenylhydrazine amount.

The molecular weights obtained ($\overline{Mv}$) are the following :

17,000	for 4.10^{-4}	mole of	reagent/g of	rubber
10-12,000	" 6.10^{-4}	"	"	"
8,000	" 8.10^{-4}	"	"	"
9,000	" 10.10^{-4}	"	"	"
8,000	" 12.10^{-4}	"	"	"

It seems that the level of molecular weights ($\overline{Mv}$ = 8,000) is a limit and that using larger amounts of phenylhydrazine does not bring any interesting result, in view of the extra cost originated.

2.2.5. Influence of the method of phenylhydrazine introduction

Depolymerization kinetics shows a rapid drop in molecular weight in the first 5 to 8 reaction hours, where it reaches 25,000-30,000 (figure 2.3).

It could be assumed that initiating the reaction by a lower amount of phenylhydrazine followed by successive additions of other variable portions to reactivate this quick degradation process, would give rubber of lower molecular weight, with the same amount of phenylhydrazine.

Experiments have been performed to that end : introduction of phenylhydrazine in several times, spaced by variable intervals and in various proportions, as indicated by figure 2.4.

Reaction parameters are as follows :

- phenylhydrazine : 6.10^{-4} mole/g of rubber
  * 2 tests with 4 and 8.10^{-4} mole/g
- temperature : 65°C
- time : 24 hours

Table 2.11

EFFECTS OF PHENYLHYDRAZINE RATIO AND AIR FLOW ON DEPOLYMERIZATION REACTION (CENTRIFUGED LATEX) - MOLECULAR WEIGHTS ($\bar{M}v$)

Fixed conditions : Latex concentration : 30 %
Reaction temperature : 65 °C
Reaction time : 24 h

Air Flow (l/mn) / Phenylhydrazine mole/g rubber	1.5		2.5		4.5	
12×10^{-4}			L.33 L.50	7,700 8,900		
10×10^{-4}			L.32	9,300		
8×10^{-4}	L.29 L.42 $L.49_1$ $L.49_2$	12,000 6,400 10,900 11,200	L.7 L.11 L.31 L.25	7,500 8,900 8,600 7,900	L.30 L.41	8,500 7,130
6×10^{-4}	L.44 L.47	9,820 9,920	L.40 L.36 L.37 L.40b	12,700 10,400 10,200 9,930	L.43 L.46	9,540 11,700
4×10^{-4}	L.45 L.51	15,300 16,700	L.38 L.35 L.38b	17,500 17,000 16,700	L.39 L.48	13,400 13,500

$L\ 49_1$ - $L\ 49_2$: Duplicate measure on the same sample
L 36 : Addition of phenylhydrazine in 2 times (50/50 - 8h30)
L 37 : Addition of phenylhydrazine in 3 times (1/3 - 1/3 - 1/3 - 4h30)

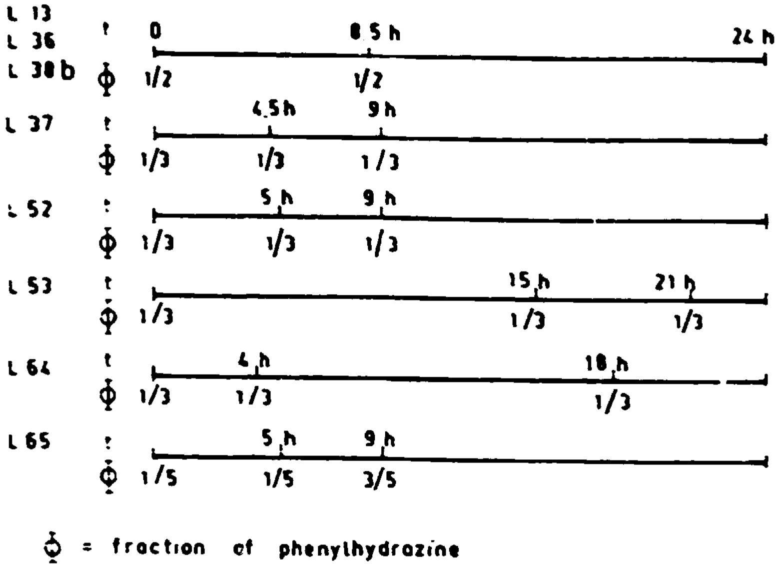


Figure 2.4.

Diagram of different methods of phenlyhydrazine introduction

The results given in Table 2.III show once more that rubber depolymerization state depends on phenylhydrazine amount;the method of introduction has no incidence on the physico-chemical properties of the product obtained, provided that the last portion is not added too soon before the end of the reaction (test L.53).

A large number of these optimization studies have been carried out on both centrifuged and field latex.

The results obtained are identical, either in the laboratory or in the pilot unit, as shown for instance by Table 2.IV which compares the rubber obtained under the same conditions in the laboratory, from centrifuged and field latex : the molecular weights obtained are identical.

It should however be noted that the liquid rubber obtained in the small pilot unit has a higher molecular weight than the liquid rubber achieved under the same conditions in the laboratory.

10,000 - 11,000 instead of 8,000 (for 8.10^{-4})
15,000 - 20,000 " 10,000 (for 6.10^{-4})

The same observations apply to the liquid rubber obtained in the pilot unit (see the tests of De Diétrich pilot and the results obtained in the Ivory Coast).

Table 2.III : EFFECT OF CONDITIONS OF PHENYLHYDRAZINE ADDITION

Reaction conditions :

- latex concentration : 30 %
- reaction temperature : 65 °C
- reaction time : 24 hours
- air flow : 2.5 l/minute

$\varphi NH-NH_2$ mole/g rubber x 10^4	Test number	Number of introductions times	$\bar{M}v1$	$\bar{M}v2$	$\bar{M}v3$	$\bar{M}v$ for 1 time
4	L 38 b	2		16,700		17,000
6	L 36	2	28,300 (8.5)	10,400		10,000
	L 37	3			10,200	
	L 52	3	54,300 (5)	23,800 (9)	10,400	
	L 53	3	35,000 (15)	21,700 (21)	12,600	
	L 64	3	61,900 (4)	14,400 (18)	10,100	
	L 65	3	77,400 (5)	28,400 (9)	9,910	
8	L 13	2	27,600 (8.5)	8,400		8,000

$\bar{M}v$ 1 = Molecular weight before second introduction

$\bar{M}v$ 2 = Molecular weight before third introduction or final molecular weight with 2 introductions

$\bar{M}v$ 3 = Final molecular weight with 3 introductions

Table 2.IV

COMPARED DEPOLYMERIZATION OF FIELD AND CENTRIFUGED LATEX

Reaction conditions : Latex concentration : 30 %
Reaction temperature : 65 °C
Reaction time : 24 h Air flow : 2.5 l/mn

Test number	L 55	L 54	L 23	L 57	L 61
Phenylhydrazine mole/g rubber $\times 10^{4}$	4	6	8	8	8
Note			3 repetitive tests 3 different samples of latex		
$\overline{M}v$ (LNR from field latex)	15,500	10,400	7,930	7,900	7,9[illegible]
$\overline{M}v$ (LNR from centrifuged latex)	17,000	10,000	← 8,000 →		

2.3. COMPLEMENTARY EXPLANATIONS

In addition to the study of the conditions directly related to depolymerization reaction, a few points were worth examined.

2.3.1. Influence of the material involved in De Diétrich reactors

As all the reactions were conducted in glass-reactors, it was necessary to check whether stainless steel, used to build the pilot unit reactors, modified the kinetics of polyisoprene degradation.

Depolymerization was carried out in the presence of a large sample of stainless steel introduced in the reaction medium.

The results obtained are identical.

2.3.2. Anti-froth influence

High anti-froth doses may be required, depending on the field latex supplies involved.

It has been demonstrated that with markedly higher amounts (5 times more than usual), depolymerization was not inhibited. Only a slight reduction in effectiveness was observed ($\overline{M}v$ obtained : 11,500 instead of 8,000). It should however be noted that this difference remains within the limits of reproductibility and that this situation is not likely to be repeated, unless an accident happens.

2.3.3. Drying conditions

In the laboratory, drying is usually achieved under vacuum at 80°C. It was checked that accidental prolongation of heating at 120°C during one hour at atmospheric pressure (presence of air), followed by a one-hour period at 120°C under vacuum, did not affect the molecular weight of the rubber obtained :

$\overline{M}v$ 13,100 instead of 12,600.

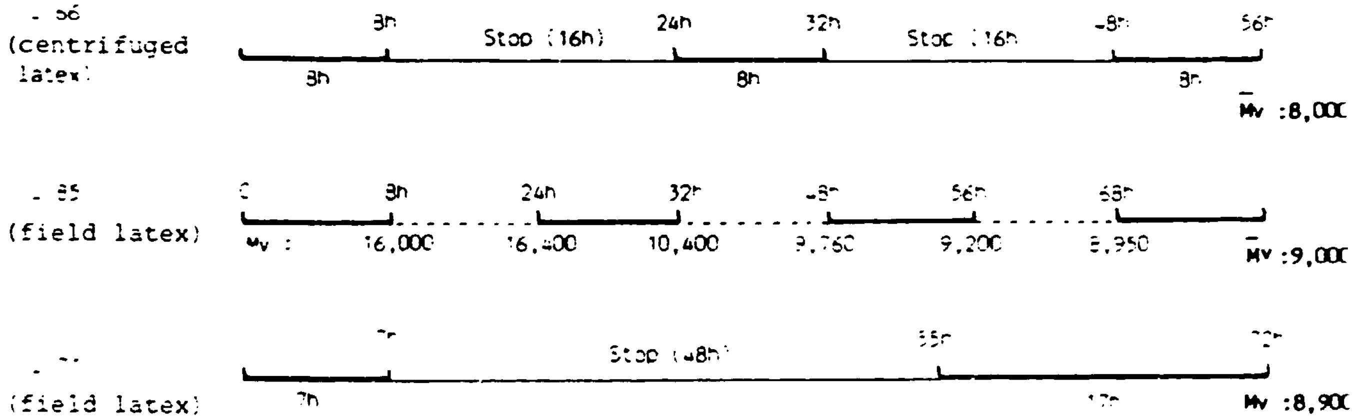
2.3.4. Simulated interruption of the depolymerization pilot unit

As interruptions of power supply are to be feared on the site of the Côte d'Ivoire , making heating, agitation and ventilation stop, simulated breakdowns have been transposed to the laboratory, on a standard depolymerization reaction.

phenylhydrazine	8.10^{-4} mole/g of rubber
temperature	65°C
effective reaction time	24 hours

The sequences of reaction interruption and starting up are illustrated by figure 2.5 :

Figure 2.5
Effect of discontinuous running of depolymerization reaction on molecular weight



- depolymerization over three 8-hour days with total interruption each night (16 hours) test L.66

- depolymerization over three 8-hour days with interrupted agitation and ventilation, and maintained heating at 65°C - test L.85

- depolymerization with a total 48-hour interruption after continuous running of 7 hours and reactor starting up during 17 hours - test L.71

Polyisoprene degradation has not been affected by these deliberate interruptions.

As a few faults had been encountered during the first tests carried out with the pilot unit of the Côte d'Ivoire(difference in the molecular weight of the final rubber as compared with pre-drying values - increase in molecular weight between depolymerization interruption and reactivation several hours after), another reaction has been conducted under extreme conditions, on the field latex involved :

- nightly interruption of agitation and ventilation with temperature maintened at 65°C,

- pre-drying ambient air relaxation period of the decanted coagulum at 65°C during 20 hours,

- continued drying under vacuum at 85°C during 4 hours after the normal 4-hour period of time.

The liquid rubber obtained has the same physico-chemical properties ($\overline{M}v$: 9,000) as those achieved under ideal conditions (continuous 24-hour reaction with no interruption whatever).

Besides, no significant increase in molecular weight is detected after night interruptions.

2.4. QUALITY CONTROL

2.4.1. Determination method of rubber depolymerization degree :

Method founded on LNR solution flowing-time

A relatively fast and simple method has been definitively established.The depolymerization degree of latex rubber can be now determined before the ultimate stages of coagulation, washing and drying, by measuring the capillary flowing-time of a rubber-solution.

Method proceeding :

- a very small latex sample (15-20 ml) is coagulated and thoroughly washed with aceton; almost all the water is eliminated, and drying becomes easier contrary to what happens with acetic or formic acid;
- a layer of LNR,as thin as possible, is spread on a cupel and dried at 100°C in a ventilated oven; complete drying is thus obtained in 30-45 mn.;
- a solution is prepared with 1,25 gr. of dry LNR in 25 ml. of toluene;
- the flowing-time of this solution is measured with a conventional viscosimeter UBBELHODE (SCHOTT-MAINZ; norm. ASTM, with capillary Ob; Ø : 0.46 mm) at 40 ± 0,2 °C;
- a calibration curve (figure 2.6) has been drawn from about 15 LNR samples of molecular weight between 7,600 and 23,000; it gives the viscosimetric weight $\overline{M}v$, vs the flowing-time.

It takes about 1 h 30 to perform the test. Perceiving the LNR molecular weight difference between $\overline{M}v$ 15 and 20,000 is quite easy, the flowing-time corresponding space being about 1 mn.

Figure 2.6 Determination method of depolymerization stage of rubber

Calibration

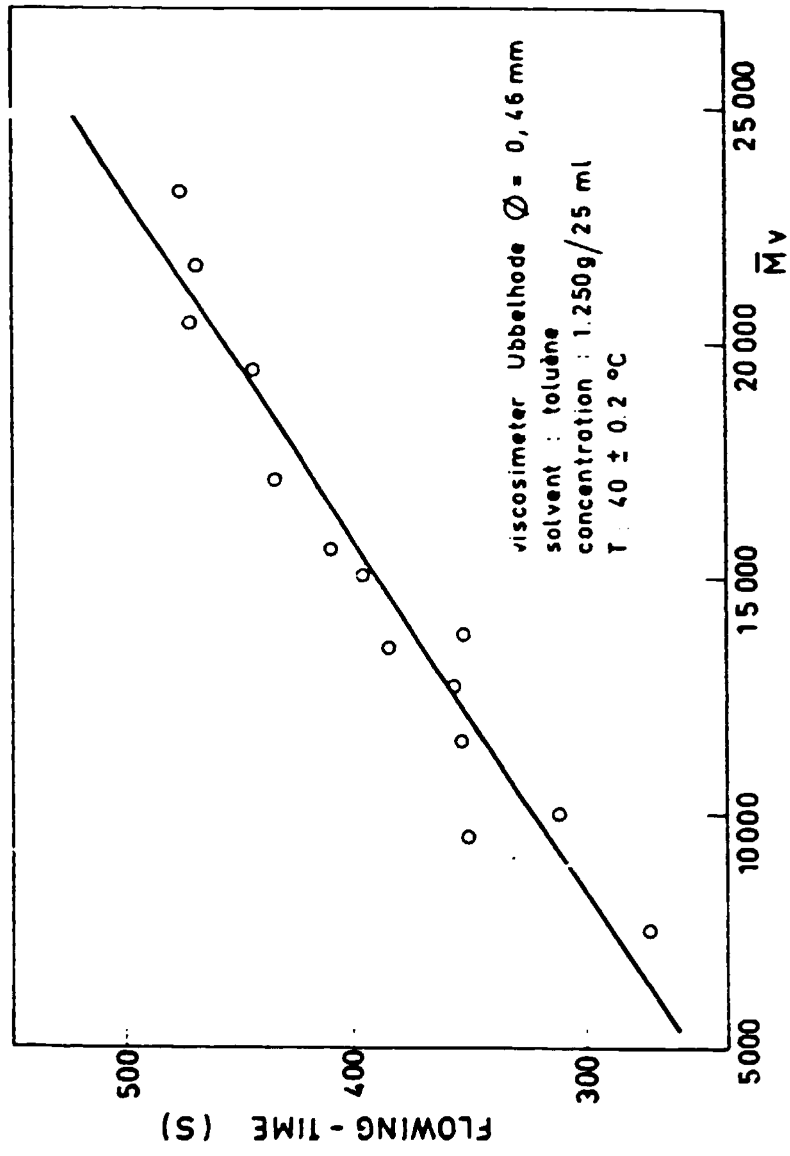


Table 2.V gives some idea on the accuracy of the method, according to the error that may be made in sample weighing.

Weight (g)	Flowing-time (s)	Determined $\overline{Mv}$	Real $\overline{Mv}$
1.250	355	12,000	11,400
1.240	342	11,300	
1.300	362	12,800	
1.340	377	13,900	

Table 2.V : Effect of an error in weighing on the precision

2.4.2. Determination of the viscosimetric molecular weight $\overline{Mv}$ in the final product - Calculation of K and a, coefficients of the MARK-HOUWINK equation with a toluene temperature of 35°C

The average viscosimetric molecular weight $\overline{Mv}$ is determined from the limiting viscosity number, in application of the MARK-HOUWINK equation :

$$[\eta] = K \, \overline{Mv}^{\,a}$$

The limiting viscosity number is defined by :

$$[\eta] = \lim_{c \to 0} \frac{\eta - \eta_o}{\eta_o C}$$

where η_o is the viscosity of the solvent
η, the viscosity of the polymer solution
C, is the dry content of the solution.

K and a are constants depending simultaneously on the polymer solvent and solvent temperature.

IRAP viscosimetries are performed on an automatic viscosimeter. However during the stay of M. Laigneau (IRCA), a manual process has been demonstrated as being possible, with the same UBBELHODE viscosimeter used to determine the depolymerization degree of rubber.

$\overline{Mv}$ is obtained with K = 0,000 502 dl/g.
and a = 0,667

toluene temperature being 25°C.

Considering the climatic conditions of the Côte d'Ivoire (ambient temperature : 30°C), K and a were calculated, the viscosity test being performed in toluene at 35°C.

Limiting viscosimetry numbers $[\eta]$ have been determined at 35°C in toluene, for 3 LNR of known weight (8,010, 15,400 and 19,200). They are shown in table 2.VI.

$\overline{M}v$	$[\eta]$	
	At 25 °C	At 35 °C
8,010	0.201	0.194
15,400	0.312	0.298
19,200	0.361	0.342

Table 2.VI : **LIMITING VISCOSITY NUMBERS OF 3 LNR AT 25 AND 35°C (solvent : Toluene)**

These three values of $[\eta]$ at 35°C make it possible to draw the following straight line :

Log : Log K + a Log M

The slope corresponds to a, and the original ordinate to Log K.

At 35°C in toluene, we have K = 0.000 561 dl/g
a = 0.650.

2.5. RESIDUAL PHENYLHYDRAZINE CONTENT AND TOXICITY

In view of the fact that phenylhydrazine is a very poisonous chemical and is described as a "highly toxic" and a "cancer suspect agent" in the Aldridge catalogue, and as LNR may be passed to industry for further trials, it is necessary to have as much analytical information as possible.

Gas liquid chromatography suggested that there might be as little as 50 ppm of free phenylhydrazine in LNR. Tests concerning dermatose induced by LNR are negative.

2.6. CONCLUSION

During this study, all the parameters involved in the reaction of natural rubber depolymerization have been examined, together with a few others more specifically related to the way the pilot plant itself works.

The technical data emerging from this study are accurate enough to ensure the smooth running of the pilot plant established in the Côte d'Ivoire.

CHAPTER - 3

COMMISSIONING TESTS OF THE PILOT PLANT

3.1. Objective of the tests

These tests were comprised in the heading "Commissioning tests" of the contract, in order to check, before loading and in presence of the representatives of UNIDO, IRCA and IRAP and of one of the IRCA engineers in charge of the project in Côte d'Ivoire,the conformity of the process and the proper working of the equipment to bring possible modifications.

The subcontractor De Dietrich Company had set the pilot plant in the "chemical engineering" shed of the factory.

3.2. Testing conditions

Two tests have been performed : one on centrifuged latex, since the procedure was well-known, and the other on field latex, to attempt to reproduce the conditions in which the depolymerization reaction will work in Côte d'Ivoire.

The equipment used differed from the unit which will be mounted in Ivory Coast only in the insulation which was not installed yet ; furthermore, external temperature (between 10 and 17° C) as well as water temperature (15° C) will be different.

3.3. Tests on centrifuged latex from October 5 to 10, 1984 (see Fig.5.1. p. 38)

A. Stabilization : the centrifuged latex (DRC 60 %) brought in 200 l. tanks has been diluted, to reduce DRC to 30 % by adding 365 l. of water, and homogenized.

The latex (730 kg or 753,3 l.) has been filtered and transferred in reactor B01 : soda (0,2 % to the dry rubber) and Nekal BX (1 % to the dry rubber) have been added and the product has been agitated for 66 hours (mechanical stability higher than 540 s).

B. Depolymerization : having the product been transferred by a vacuum pump from reactor B01 to R02 (T = 60° C), phenylhydrazine was introduced. As a matter of fact this was not done as expected (i.e. by the same circuit as air and at the same time) since the pipe choked after the demixion of phenylhydrazine and its cristallization in the cold pipe. The remaining phenylhydrazine was introduced directly through the reactor inspection hole (9 % or 17,2 l. in 50 l. of water) ;

a modification has been allowed : creation of a phenylhydrazine independant circuit. A night watch has been kept to control foaming : 450 cc. of anti-foaming agent Rhodorsil have been introduced during depolymerization. After a 23 hours reaction, depolymerization has been controlled according to the procedure described page 13, giving a viscosimetric mass of around 10,000.

C. Coagulation - washing - drying : having the product been transferred by a vacuum pump from RO2 to RO3, acetic acid was introduced (4 % to the dry rubber) ; after decantation and drawing off of 225 l. of water, four successive washings have been performed. The introduced and removed water quantities are given below :

	introduced water quantity	removed water quantity
1st washing	200 l.	87,5 l.
2nd washing	150 l.	95 l.
3rd washing	150 l.	115 l.
4th washing	150 l.	133 l.

Drying has been carried out maintaining the product temperature at 60° C under a vacuum of 150-160 mm Hg. At the end of the drying process (after 15 h) pressure decreases and temperature rises ; 230 kg. LNR of $\overline{M}v$ mass : 11,100 have been drawn off.

Characteristics of the rubber obtained :

Mv : 11,100
Mw : 44,200
Mn : 7,500
I : 5.9
N^{2} % : 0.49
volatile matter : 0.45 %

3.4. Tests on field latex from October 15 to 17, 1984

A. Stabilization : the field latex (730 kg. at 30.5 % DRC) from Ivory Coast has been filtered and poured into reactor BO1 ; soda (0.2 % to the dry rubber) and Nekal BX (1 % to the dry rubber) have been added and the product has been agitated for 55 hours (mechanical stability higher than 540 s).

B. Depolymerization : the product has been transferred in reactor RO2 (T = 63° C) in which phenylhydrazine has been introduced (9 % or 19.26 kg in 50 l. of water) ; foaming has been quickly controlled by adding an anti-foaming agent : 650 cc ; a night watch has proved indispensable. After a 24 hour reaction, depolymerization has been controlled giving a viscosimetric mass of around 9,500.

C. Coagulation - washing - drying : having the product been transferred to reactor RO3, acetic acid was introduced (6 % to the dry rubber) ; after decantation and drawn off of 315 l. of water, three successive washings took place. They are summarized in the following table :

	introduced water quantity	removed water quantity
1st washing	400 l.	378.5 l.
2nd washing	200 l.	198 l.
3rd washing	200 l.	217 l.

Drying has been carried out maintaining the product temperature at 60° C under a vacuum of 140-150 mm Hg. At the end of the drying process, (after 10 h.) 240 kg LNR of $\overline{M}v$ mass : 11,300 have been drawn off.

Characteristics of the rubber obtained :

Mv : 11,300
Mw : 44,400
Mn : 7,130

I : 6.2
N^2 % : 0.88
volatile matter : 0.90 %

3.5. Conclusion

Both tests are satisfactory indeed : 230 kg. and 240 kg. have been produced without difficulty. Thanks to a fruitful collaboration between IRAP, De Dietrich and IRCA, this semi-industrial unit was operational and able to produce a representative amount of LNR.

Having been modified, the plant has been heat-insulated, dismantled and packed according to the schedule provided by De Dietrich. It reached Côte d'Ivoire early January, date at which reassembly started.

CHAPTER - 4

SETTING UP OF THE PILOT PLANT
IN COTE D' IVOIRE

4.1. CIVIL WORKS

4.1.1. Introduction

According to the sequences of IRCA's programme, the construction of a factory building which is destined to shelter the pilot plant has been carried out during April, May, June and July 1984.

This pilot plant, mainly composed of reactors (1,200 l.), is 25 square meters and 6 meters high. It was therefore necessary to build an edifice large enough to shelter the pilot plant as well as different outbuildings such as a raw material store, spare parts stores, etc.... In addition to constructions existing before, we have decided to build a structure of about 150 square meters which will gather the different stores and the pilot plant. The laboratory will be established in a structure already available.

4.1.2. Site selection

Following criteria were taken into consideration for best possible settlement of the pilot plant building :

- unity of locality
- surroundings
- security
- approach ways
- prices
- delays.

4.1.3. Building contractor's selection

Six metal frame and civil engineering builders have been contacted ; only one was selected for his serious references and his competitive prices : SAMELA Company-01 B.P. 1177 - Abidjan 01 - Côte d' Ivoire.This metal frame builder has subcontracted the civil engineering works to the Company IVCO-04 B.P. 911 - Abidjan 04 - Côte d'Ivoire.

4.1.4. Civil engineering works chronology

Civil works started on May 15th, 1984, after the development plans have been drawn.

ETECO Company-01 - B.P. 1687 - Abidjan 01 (engineering company) designed the civil engineering plans.

The edifice of the pilot plant has the following specifications : 18 m. long, 9 m. wide, 7 m. high. IVCO Company has started the civil engineering works by the levelling. Then, excavations, solid mass, and longitudinal beams successfully followed.

Then the frame, consisting of four truss of roof, has been set up on ten I-poles. Only after having fixed the rails on the poles, these could be bedded. A coat of paint with tar has been deposited on the side of the rails in contact with boarding so as to avoid any electrolysis phenomena. The ciphering grids have been buttwelded on the higher part of the building, up to one meter high in order to permit a natural ventilation of the building.

The roof, composed of aluminium sheets and transparent polyester sheets for zenithal lighting, has been fixed to the rails as well as the lintels of the door to the poles.

Then the reinforced concrete flag has been pourred, with its reservations for gullies and for the I-poles of the pilot frame.

The civil engineering works concluded with the erection of a low wall (0,6 m. high) along the circumference of the building. After two coats of grey paint, the boarding and polyester sheets have been fixed. The head work and electricity ended the construction of the building.

Provisory acceptance test took place on July 30th, 1984, according to the time schedule.

Pictures n° 1 and n° 2, page 27, show the outside and the inside of the building.

4.2. PILOT PLANT SETTING UP

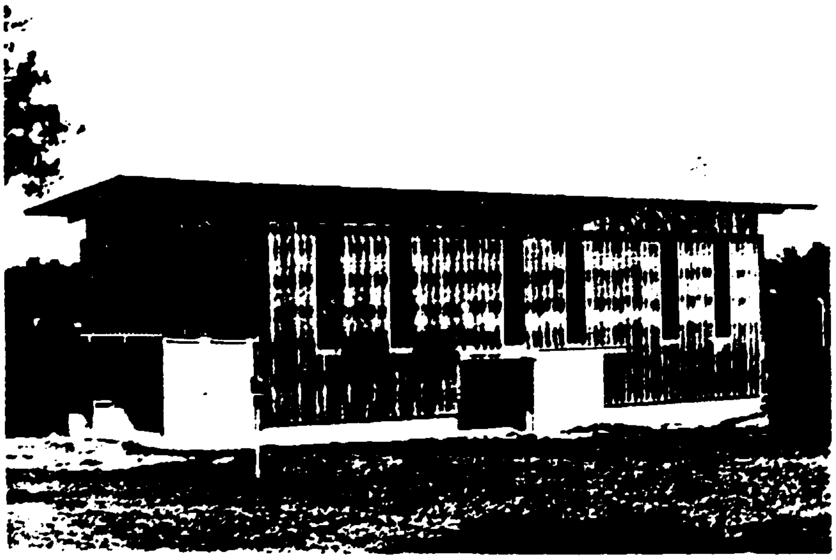
After the pilot had been given trials at De Dietrich in France, it has been dismantled, put into a container and shipped to Ivory Coast by boat. The "Yolande Delmas" arrived on January the 2nd, 1985 in Abidjan. Then, after clearance of goods, the container was transferred and received at IRCA Bimbresso on January 22nd. The frame of the pilot plant was built by experts within a week.

Then two tanks and one condenser have been fixed on the first floor as well as the electrical dispatching assembly. Different tanks and pumps have been set up as well as the electric boiler and the compressor.

One month time was necessary to plug in connection different electric motors and to install pipe and tube works. Water has been given a trial in order to test the pilot plant water-tightness.

Production of liquid natural rubber started on April 9th, 1985.

I - Inside view



2 - Pilot plant building outlook

4.3. EMERGENCY GENERATOR

Considering the unceasing electricity cuts in Côte d'Ivoire prejudicial to the project (some reactions must be carried out during 24 hours without interruption), Republic of Germany has answered positively to our request giving supplementary estimates to buy an emergency generator.

These characteristics are :

. Diesel motor DEUTZ F 6L 413 FR
  - power : 89 kw
  - speed : 1,500 rpm

. Alternating current generator
  - power : 100 kva
  - cosine φ : 0,8
  - voltage : 380 V
  - frequency : 50 hz

This emergency generator has been shipped to Côte d'Ivoire by boat. The "Bonake" arrived on April 12th. Then, after clearance of goods, it was set up in IRCA Bimbresso.

Modifications were necessary in the electrical station.

The emergency generator provides 15 % (on an average) of the plant's energy.

4.4. STARTING UP

4.4.1. Description (see in annexe general layout of the pilot plant)

The pilot plant is mainly composed of three tanks taking in respectively the reaction of stabilisation, depolymerization and coagulation/drying.

- Stabilization tank B01

. specification :
  - polypropilene
  - diameter : 1,200 mm
  - depth : 1,590 mm
  - total volume : 1,200 l.

. equipment :
  - stirrer, speed : 150 rpm
    power : 0,37 kw

- Depolymerization tank R02

. specification :
  - stainless steel
  - diameter : 1,200 mm
  - total volume : 1,670 l.
  - duty pressure : - 1 to + 3 bars

. equipment :
- stirrer, speed : 175 rpm
  power : 1,5 kw
- safety valve
- calibrated valve
- thermometer
- manometer
- heater coiled tube

- Coagulation / Washing / Drying tank RO3

. specification :
- stainless steel
- diameter : 1,200 mm
- total volume : 1,670 l.
- duty pressure : - 1 to + 3 bars

. equipment :
- stirrer, speed : adjustable
  power : 5,5 kw
- safety valve
- thermometer
- manometer
- heater coiled tube
- condenser, type FX 273.10.1.H
  output : 2,2 m^3/h
  surface : 6 m^2
  duty pressure : 3 bars

- Supplement

. Compressor CO16
type : Px 20/100 H
output : 11 m^3/h
power : 2 cv
duty pressure : 3 bars

. Electric boiler CHO6
type : RH 440.80.0
power : 80 kw
temperature : 250° C

. Vacuum pump PVO8
type : water ring
speed : 2,800 rpm
power : 1,5 kw
output : 43 m^3/h

. Pumps
type : moto-variateur
speed : 1,500 rpm
power : 0,25 kw
output : 50 - 200 l/h

type : moto-variateur
speed : 1,500 rpm
power : 0,9 kw
output : 50 - 200 l/h

. Phenylhydrazine tank B04

- specification : stainless steel
  diameter : 570 mm
  depth : 800 mm
  total volume : 150 l.

- stirrer, speed : 1,500 rpm
  power : 0,18 kw

. Acetic acid tank B05

- specification : polypropilene
  diameter : 460 mm
  depth : 450 mm
  total volume : 60 l.

- stirrer, speed : 1,000 rpm
  power : 0,18 kw

. Distillate water tank RE17

- specification : stainless steel
  diameter : 800 mm
  depth : 1,000 mm
  total volume : 400 l.
  duty pressure : 3 bars

. Flow-meter

. Tubes

. Taps

. Electric switchboard

4.4.2. Process instructions

4.4.2.1. Stabilization

Latex is transferred from drums (200 litres) to the tank B01 through compressed air.

For this operation :
- put the special cap on the top of the drums full of latex,
- plug the tubes for air admission,
- plug the tubes for flowing out of latex,
- check : a. the drain cock n° V40-146 is turned off
  b. the compressor C016 is turned on,
- open the tap of air admission regulation so as to keep always under pressure 0,2 bars,
- execute the same operation for the 4 drums,
- clean drums and tubes after transfer,
- start up the stirrer of tank B01.

4.4.2.1.1 Transfer from tank B01 into tank R02

- Check the filter n° V40.127 is cleaned.

- Check that :

  - . V32.104 is turned off,
  - . the introduction of antifoam agent is turned off,
  - . the introduction of phenylhydrazine is turned off,
  - . V40.103 is closed,
  - . the tank R02 scuttle is closed.

- Start up the electric boiler (3 resistances, temperature 100° C).

- Check that :

  - . the thermic fluid tap R02 is turned on,
  - . the thermic fluid tap R03 is turned off,
  - . the thermic fluid by-pass is turned off.

- Start up the vacuum pump after water admission has been turned on and after having checked that V32.116 has been turned off.

- Check that :

  - . the distillate water tank is closed,
  - . the tap V32.109 of the vacuum pump is turned on.

- Open the tap V32.121 after the scuttle has been closed.

- Check the pressure on the manometer (400 mm Hg).

Latex admission :

- open the taps V40.101 and V40.145,

- adjust the latex delivery so as to obtain as less foam as possible by handling taps V8.115 and V32.121 if necessary,

- when the transfer is over :
  - . turn off the taps V40.101, V40.145 and V32.121,
  - . switch off the vacuum pump,
  - . open the tap V32.104,
  - . start up the compressor and the stirrer of tank R02,
  - . adjust air compressed admission with the tap V15.119.

Preparing of phenylhydrazine solution :

- tank B04 has to be cleaned,

- the drain cock V15.147 has to be turned off,

- the thermic fluid tap V15.125 is turned on,
- adjust the temperature of electric boiler to 100° C,
- pour 50 l. of water into tank B04 and 18,6 l. of phenylhydrazine,
- start up the stirrer of tank B04.

4.4.2.2. Depolymerization

enylhydrazine solution admission :

- check :
  - . the temperature of latex is about 65° C in tank R02,
  - . the temperature of phenylhydrazine solution is about 50° C in tank B04,
  - . the stirrer of tank R02 is started up,
  - . V15.141 is turned off,
  - . V15.149 (phenylhydrazine solution admission) and V15.118 are turned on,
- start up the electric pump PD 14 at its upper delivery,
- after transfer turn off V15.149.

Depolymerization :

- adjust air bubbling with the tap V15.119,
- add antifoam by the tap V32.139 according to the quantity of foam making,
- swill down the pump PD 14 and the tubes used for the transport of phenylhydrazine solution.

Transfer from tank R02 into tank R03

- Check : . the tank R03 and the filter V40.120 are cleaned,
  - . the drain cock V50.108 of tank R03 is turned off,
  - . the drain cock V40.102 of tank R02 is turned off,
  - . the thermic fluid tap V32.107 is turned on,
  - . the tap V10.124 is turned on.
- Start up the vacuum pump.
- Check : . V32.121 is turned off,
  - . V25.111 " " "
  - . V8.115 " " "
  - . V8.112 " " "

  - . V32.109 is turned on,
  - . V32.116 " " "
  - . V40.120 " " "
  - . V40.103 " " ".

- After the transfer, stop the vacuum pump and turn off V40.103 and V40.120.

- Check V8.112 is turned on.

Preparation of acetic acid solution :

Check : . the tank B05 is cleaned,
. the tap V15.117 is turned off,
. the tap V15.140 is turned off,
. start up the stirrer of tank B05,
. pour 10 l. of acetic acid and 10 l. of water into tank B05.

4.4.2.3. Coagulation - Washing

- Check the tap V15.117 is turned on.

- Start up the electric pump PD 15.

- After transfer, wait 10 mn and start up the electric stirrer MA13 of tank R03.

- Swill down the pump PD 15 and the tubes used for the transport of acetic acid.

- After decantation draw off the water with the tap V50.108.

Washing :

- open the taps V15.114 and V15.113,

- turn off those taps when have been introduced respectively :

  . 400 l. of water for the first washing,
  . 200 l. for the second washing,
  . and 200 l. for the third washing,

- draw off by the drain cock V50.108.

4.4.2.4. Drying

- Check . V32.121
  . V25.134
  . V32.106
  . V25.132

  are turned off.

- Start up the electric boiler, temperature : 120° C.

- Check
  - . V32.116
  - . V25.111
  - . V15.148
  - . V20.137

  are turned on.

- Start up the electric stirrer MA13 and the vacuum pump.

- Adjust the temperature of water Ths 07.
  A rising of temperature, a higher vacuum and a dark color for the rubber are characteristics of the end of the drying.

- Stop the electric boiler and the vacuum pump.

- Open V8.112 and V50.108.

- Draw off the liquid natural rubber.

Some views of the pilot plant are given in Annex 1.

OPERATING INSTRUCTIONS

TAPS N°	FUNCTIONS	Stabilization	Transfer into RO2	Depolymerization	Swelling down phenylhydrazine tubes	Transfer into RO3	Coagulation	Swelling down acid tubes	Washing	Decantation	Drawing off water	Drying	Drawing off rubber
		OPERATIONS											
V40.146	Drawing off BO1	C	C	.	.	.	.	.	.	.	.	.	.
V40.101	Connection BO1-RO2	C	O	.	.	.	.	.	.	.	.	.	.
V40.145	Antireturn foam	C	O	C	C	C	.	.	.	.	.	.	.
V15.119	Bubbling air	C	.	R	R	R	C	C	C	C	C	C	C
V32.104	Ventilation RO2	.	C	O	O	O	.	.	.	.	.	.	.
V32.139	Admission antifoam agent	.	C	O	O	.	.	.	.	.	.	.	.
V8.130	Removing steam on the scuttle RO2	C	C	O/C	O/C	O/C	C	C	C	C	C	C	C
V15.149	Introduction phenylhydrazine	C	C	O	O/C	C	.	.	.	.	.	.	.
V32.121	Vacuum RO2	.	O	.	.	C	.	.	.	.	.	C	C
V40.103	Bottom tank RO2	C	C	C	C	O	.	.	.	.	.	.	.
V40.102	Drawing off RO2	.	C	C	C	C	.	.	.	.	.	.	.
V40.120	Separating RO2-RO3	.	.	.	.	O	C	C	C	C	C	C	C
V32.106	Thermic fluid RO2	C	O	O	O	C	C	C	C	C	C	C	C
V15.132	By-pass thermic fluid	.	C	C	C	.	.	.	.	.	.	C	.
V32.107	Thermic fluid RO3	C	C	C	C	C	C	C	C	C	C	O	C
V15.125	Thermic fluid BO4	C	C	O	O	C	C	C	C	C	C	C	C
V15.126	Thermic fluid BO4	O	O	O	O	O	O	O	O	O	O	O	O
V15.141	Ventilation RO2	C	C	C	O/C	C	C	C	C	C	C	C	C
V15.118	Connection BO4-PD14	C	C	O/C	O	.	.	.	.	.	.	.	.
V15.147	Drawing off BO4	.	C	C	O/C	.	.	.	.	.	.	.	.
V32.109	Separating vacuum pump	.	O	.	.	O	.	.	.	.	.	O	.
V32.116	Vacuum in the condensor	.	C	.	.	O	.	.	.	.	.	O	.
V15.113	Isolation water meter	C	C	C	C	C	C	C	O/C	C	C	C	C
V15.114	Isolation water meter	C	C	C	C	C	C	C	O/C	C	C	C	C
V8.112	Ventilation RO3	.	.	.	.	C	.	.	.	.	.	R	.
V15.148	Vacuum in the distillate water tank RE 17	.	C	.	.	.	.	.	O/C	.	.	O	.
V18.131	Removing steam on the scuttle RO3	C	C	C	C	C	C	C	C	C	C	C/O	C
V18.115	Adjusting vacuum	.	R	.	.	C	.	.	.	.	.	R	.
V50.108	Drawing off RO3	.	.	.	.	C	C	C	C	C	C	C	O
V15.117	Connection BO5-PD15	C	C	C	C	C	O	O	C	C	C	C	C
V15.140	Ventilation PD15	C	C	C	C	C	C	O/C	C	C	C	C	C
V20.137	Cooled water of the condensor	C	C	C	C	C	C	C	C	C	C	O	C
V15.111	Connection CO7.RE17	.	.	.	.	.	.	.	.	.	.	O	O
V25.134	Drawing off the distillate water tank RE 17	C	C	C	C	C	C	C	O/C	C	C	C	O
V10.124	Water for vacuum pump	.	R	.	.	R	.	.	.	.	.	R	.
V15.133	Isolation of distillate water tank RE 17	.	C	.	.	.	.	.	O/C	.	.	C	.
V15.135	Compressed air	C	C	C	C	C	C	C	O/C	C	C	.	.
A.9	Stirrer BO5						M						
A.10	Stirrer BO1	M											
A.11	Stirrer BO4			M	M								
MA.12	Stirrer RO2		M	M	M	M							
MA.13	Stirrer RO3					M	M	M	M	A	A	M	M
PV.08	Vacuum pump		M			M						M	
PD.14	Phenylhydrazine pump		M/A	M									
PD.15	Acid pump						M/A	M					
CO.16	Compressor		M	M	M	M	M	M	M	M	M	M	M
CB.06	Boiler		M	M	M							M	A

Legend :			
C = the tap is closed		. = any position of the tap	
O = the tap is opened		M = the motor is on	
R = the tap is adjusted		A = the motor is off	

H	SATURDAY	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY
6 -				Heating		
7 -	Transfer of latex into the reactor BO1	Transfer from BO1 into RO2 Heating	Control test on the 5th sample	Beginning of distillation	Cleaning	
8 -			6th sampling		Maintenance	Latex collection NH_3 = 3,5 g/l
9 -	Sampling analysis : DRC, pH, NH_3	Introduction of φ NH-NH_3 , air				
10 -	Introduction of Nekal BX, soda					
11 -	Agitation/sampling Preparation of the transfer		Coagulation Decantation Drawing off			
12 -	End of agitation					
13 -		1st sampling				
14 -			1st washing			
15 -			2nd washing		Cleaning	Cleaning
16 -			3rd washing			
17 -		2nd sampling		End of the drying LNR drawing off		
21 -		3rd sampling				
1 -		4th sampling				
5 -		5th sampling				

Time schedule of a complete depolymerization

CHAPTER - 5

PRODUCTION OF LIQUID NATURAL RUBBER

5.1. PROCESS PRINCIPLE

5.1.1. Stabilization

Field latex is stabilized with the help of ammonia, caustic soda and soap, in order to give the product enough mechanical stability (tank B01). Then the latex is transferred into the depolymerization reactor (RC2) by sucking under vacuum. For the details of the layout see the figure 5.1.

5.1.2. Depolymerization

To depolymerize the latex, we need three chemicals :

- molecule of rubber
- phenylhydrazine
- oxygen (from air).

The reaction takes place at 65° C for 24 hours.

Phenylhydrazine is added, as a shot, at the beginning of the reaction. Air is bubbling for 24 hours into the latex. (Oxygen, phenylhydrazine and rubber molecule give peroxides and hydroperoxides which are not stable and by decomposition, they give shorter molecules of rubber, step by step it is possible to obtain very low molecular weight i.e. 10,000). Samples are taken during the reaction and a fast evaluation gives the molecular weight by checking the viscosity of a solution

5.1.3. Coagulation, washing, drying

After 24 hours, the depolymerized latex is transferred into the next reactor (R03) where it is coagulated by addition of acid (formic or acetic) ; the obtained coagulum is then washed three times and the drying takes place under vacuum at 55° C. When it is dried (after 10 hours), the rubber is liquid and it is poured into a drum by opening the reactor bottom valve.

5.2. LABORATORY EXPERIMENTATION

5.2.1. Laboratory pilot for feasibility studies

A small equipment has been installed, in December 1984, in our laboratory at Bimbresso, with a capacity of 1 litre of latex. It is a glass reactor with a jacket for temperature control, equipped with a pump for air bubbling during the depolymerization stage.

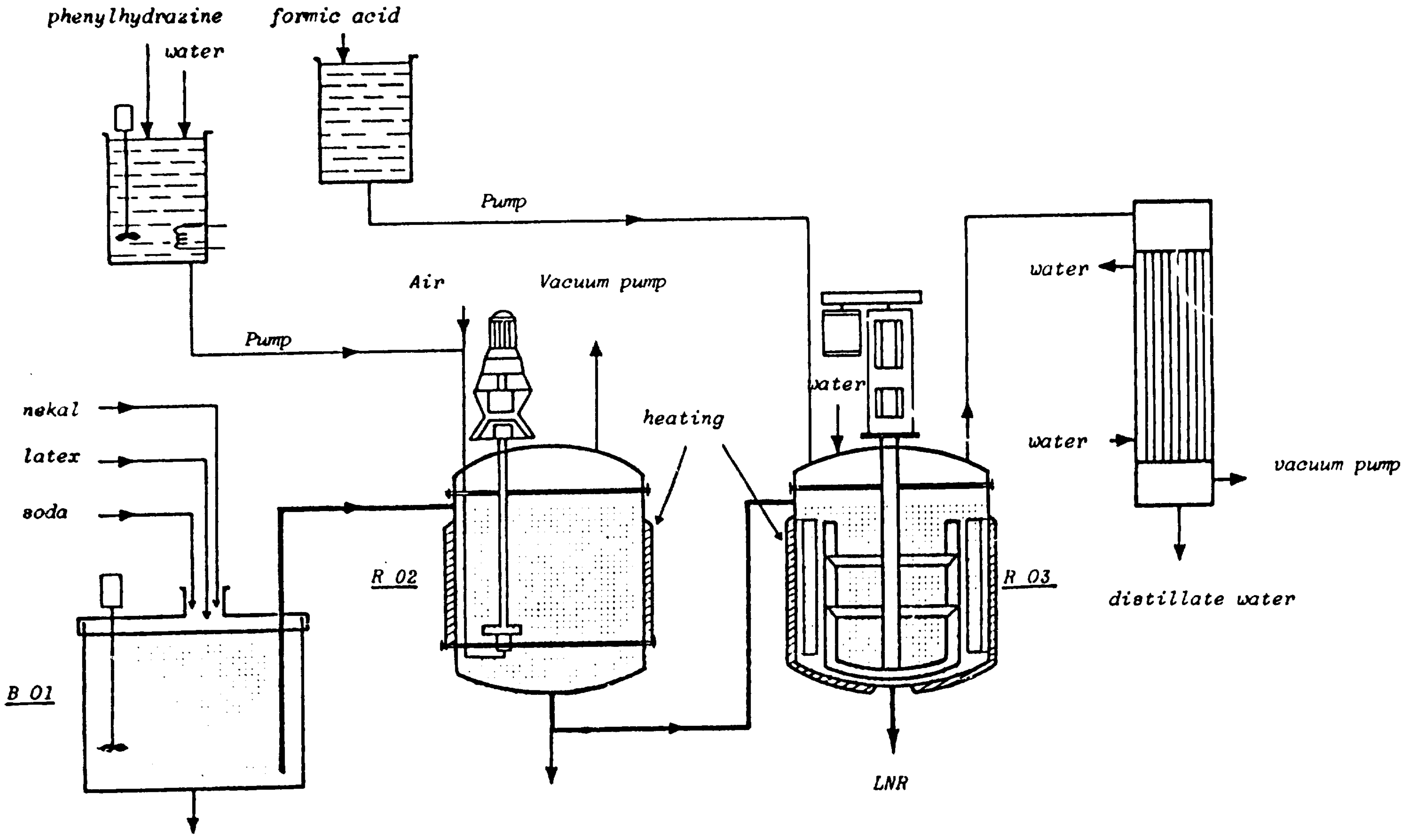


Figure 5.1. : LAYOUT OF PILOT PLANT FOR LIQUID RUBBER

The same reactor is used for coagulation, washing and drying, for the latter a vacuum pump is required and a condenser at 0° C is used to avoid water to enter the pump. This equipment (shown in figure 5.2.) was mainly designed for feasibility studies.

5.2.2. I.R.A.P.'s recommendations

The process parameters were defined based on I.R.A.P.'s recommendations :

- stabilization : after pH adjusted to 10 by ammonia (for initial preservation) addition of : Nekal BX, anionic soap, 1 % of active material based on dry rubber (% means weight percent of active material, based on dry rubber in the all chapter 5) ; and 0,2 % of caustic soda,

- reaction temperature : 60 - 70° C,

- total reaction time : 24 hours,

- phenylhydrazine : 8,64 % (standard rate),

- air flow : 2,5 l/min.

5.2.3. Fresh field latex

The latex used by I.R.A.P. was field latex preserved by ammonia (9 g/litre of latex). This high level was chosen to give the latex enough stability for shipment and storage over months. But in Côte d'Ivoire,fresh latex can be used few days after tapping ; in that case maturation cannot take place -or not at the same scale than in few months- and the latex may have a different behaviour (chemically speaking). A series of batches was made with fresh field latex without any problem and with similar results than those obtained by I.R.A.P. We can conclude that fresh field latex is suitable for depolymerization and for producing liquid rubber.

5.2.4. Influence of D.R.C.

Three batches were made with the same latex (from GT1, Anguededou plantation, stabilized with ammonia 9 g/litre of latex). The same amount of phenylhydrazine was used (standard rate) and the same reaction time (24 hours) ; but in the two first cases the latex was diluted (25 % of DRC instead of 30). If we observe the table 5.I., it seems that the lower the DRC, the lower the final molecular weight, but it is difficult with our equipment to monitor, with accuracy, the air flow and this may be a cause of variations in the final results. Anyway, this possible advantage is too small to be taken into account because, as a counterpart, we have more water to evaporate during the drying.

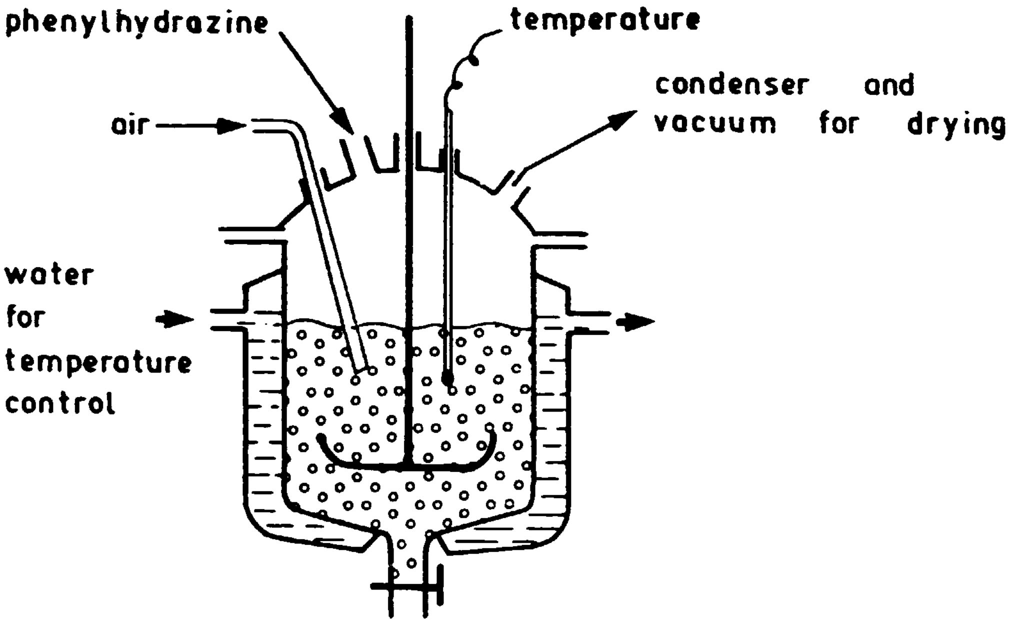


Figure 5.2. : Laboratory pilot layout

Table 5.I.

Influence of latex DRC
on depolymerization

Batch n°	Latex DRC (%)	Date of coagulation	Mv
L 18 84	25	November 30	12 650
L 20 84	25	December 14	11 450
L 21 84	30	December 21	14 350

(Latex from GT 1, Anguededou plantation, tapped on November 26, 1984)

5.2.5. Preservation study : nature and level

In order to avoid a confusion : preservation means to give the latex a protection against coagulation during storage. Stabilization means to give the latex enough mechanical stability to avoid coagulation (mechanical or thermal) during the depolymerization step. Stabilization is always the same, by caustic and soap. But preservation is a function of storage conditions and period.

Two series of trials were carried out. For the first one, ammonia was used to increase the PH (range level from 2.2 to 9.0 g/litre of latex). For the second series, after addition of soda (range from 1.6 to 7.2 g/litre of latex), the latex was blended with an emulsion of phenylhydrazine in water (an anionic soap : Nekal BX was used to obtain a better emulsion at room temperature). The pH values of all the samples are given in the tables 5.II. and 5.III.

Concerning the preservation with ammonia, a level of 3.7 g/litre is high enough to give the latex a good stability, at least during two months.

For the system "caustic-phenylhydrazine", a level of 3.6 g of soda/litre is required for a good protection during a month ; for a better stability, this level must be increased to 4.8 g/litre.

Table 5.II.

Ammonia stabilized latex

Runs n°	1	2	3	4	5	6	7
NH_3 g/l	9.0	7.5	6.0	4.5	3.7	3.0	2.2
Initial latex pH	10.15	10.05	9.90	9.75	9.70	9.60	9.35
Dates	latex pH	latex pH	latex pH	latex pH	latex pH	latex pH	latex pH
6/2	10.10	9.95	9.85	9.75	9.65	9.50	9.20
7/2	10.05	9.90	9.80	9.68	9.60	9.42	8.91
9/2	10.15	10.05	9.90	9.80	9.75	9.55	9.70
11/2	10.15	10.05	9.95	9.85	9.77	9.55	8.15
13/2	10.11	10.00	9.90	9.75	9.72	9.40	7.95
15/2	10.00	9.95	9.80	9.70	9.60	9.10	(C)
18/2	10.10	10.00	9.85	9.75	9.65	9.05	
20/2	10.02	9.95	9.80	9.65	9.55	8.85	
22/2	10.02	9.95	9.80	9.65	9.55	8.70	
25/2	10.06	9.95	9.80	9.65	9.55	8.70	
27/2	10.00	9.85	9.72	9.60	9.50	8.70	
2/3	9.98	9.85	9.72	9.58	9.50	8.85	
4/3	9.95	9.85	9.70	9.55	9.50	8.55	
6/3	9.95	9.85	9.70	9.55	9.45	8.55	
8/3	9.95	9.62	9.70	9.52	9.40	8.55	
11/3	9.85	9.85	9.73	9.52	9.40	8.50	
13/3	9.85	(M)	9.65	9.45	9.40	8.55	
15/3	9.82		9.56	9.46	9.35	8.41	
18/3	9.85		9.61	9.48	9.37	8.48	
20/3	9.84		9.60	9.49	9.36	8.46	
22/3	9.76		9.54	9.40	9.28	8.41	
25/3	9.78		9.56	9.42	9.29	8.41	
27/3	9.74		9.52	9.38	9.27	8.41	
29/3	9.68		9.46	9.33	9.05	8.37	

(C) = coagulated sample

(M) = sample destroyed by mistake

Table 5.III.

Latex stabilized with soda
and phenylhydrazine

Runs n°	A	B	C	D	E	F
Soda (g/l)	7.2	6.0	4.8	3.6	2.4	1.6
Phenylhydrazine g/l	6.0	6.0	6.0	6.0	6.0	6.0
Nekal BX (g/l)	1.0	1.0	1.0	1.0	1.0	1.0
Initial latex pH	11.85	11.75	11.50	10.45	9.35	8.35
Dates	latex pH	latex pH	latex pH	latex pH	latex pH	latex pH
6/2	11.80	11.65	10.95	10.22	9.02	6.60
7/2	11.75	11.65	11.05	10.32	7.50	(C)
9/2	11.90	11.85	10.95	10.30	(C)	
11/2	11.95	11.85	10.90	10.35		
13/2	11.80	11.70	10.72	10.15		
15/2	11.70	11.60	10.60	10.00		
18/2	11.75	11.65	10.60	10.05		
20/2	11.65	11.55	10.45	9.95		
22/2	11.65	11.52	10.45	9.85		
25/2	11.60	11.48	10.40	9.90		
27/2	11.55	11.38	10.30	9.85		
2/3	11.50	11.30	10.25	9.80		
4/3	11.40	11.20	10.15	9.70		
6/3	11.40	11.20	10.15	9.50		
8/3	11.30	11.20	10.10	9.45		
11/3	11.30	11.00	10.02	9.25		
13/3	10.95	10.75	9.85	(C)		
15/3	11.07	10.86	9.97			
18/3	11.03	10.83	9.97			
20/3	10.95	10.76	9.90			
22/3	10.89	10.70	9.85			
25/3	10.77	10.60	9.78			
27/3	10.72	10.54	-			
29/3	9.78	9.77	9.56			

(C) = coagulated sample

5.2.6. Development of a "fast evaluation method" for depolymerization

During the course of the depolymerization reaction, latex samples are taken and analyzed by a called "fast evaluation method" (coagulation with acetone and measure of the flowing time for a given solution of rubber in toluene). The last sample, just before transfer and coagulation with acid, should give an indication of the final rubber molecular weight. The "true" viscometric molecular weight $\overline{M}v$ is obtained by the standard procedure based on Mark-Houwink-Sakurada equation. Figure 5.3. shows the calibration curve between $\overline{M}v$ and flowing time.

In table 5.IV. we can see the results of the two different methods. The excellent correlation obtained allows us to consider the fast evaluation as a "routine tool" for the pilot plant.

Table 5.IV.

Batch n°	Fast evaluation (based on flowing time)	"True" Mv (based on limiting viscosity number)
L 4 84	14 800	14 750
L 5 84	11 700	11 700
L 6 84	10 800	10 850
L 8 84	9 000	8 950
L 9 84	9 000	9 050
L 10 84	19 600	19 600
L 12 84	9 000	9 050
L 15 84	11 100	11 150
L 20 84	11 400	11 450
L 21 84	14 300	14 350

Molecular weight of liquid natural rubber :

comparison of the results obtained by two different methods.

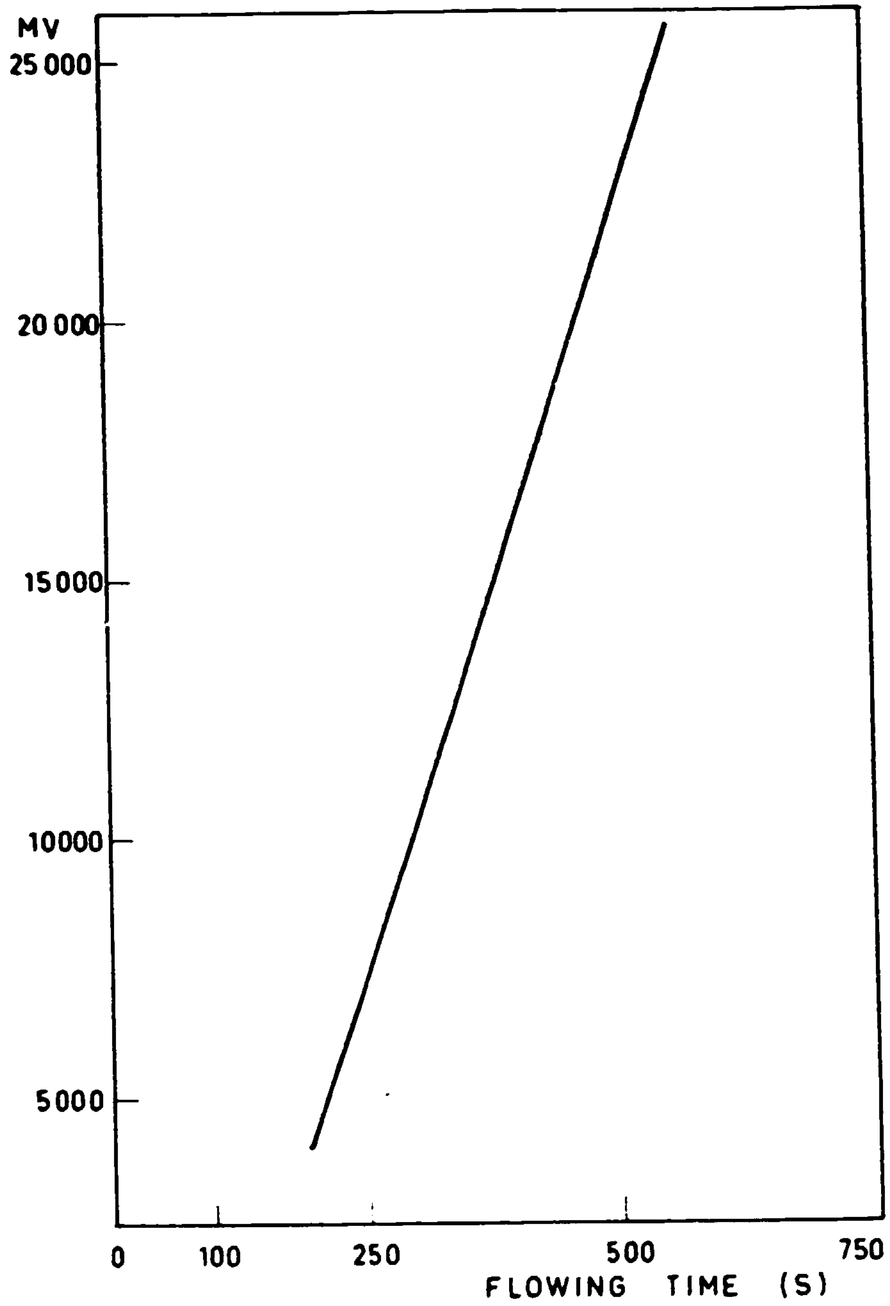


Figure 5.3. : Calibration curve between $\overline{M}v$ and flowing time

5.3. PRODUCTION

5.3.1. Latex supply : clones, preservation - chemicals

The first production batches were made with latex from Anguededou plantation (estate) ; the clones selected were GT 1 and PB S6, each week we collected around 800 litres from March to June 1985. At the end of April, we decided to use only 3.5 g of ammonia/litre of latex instead of 9.0 for preservation (based on the previous laboratory study) and, as expected, the system is satisfactory. In July, a part of IRCA's plantation was equipped with new cups and since that time, latex used for producing liquid rubber is coming from our own plantation (ex. seedling). The average amount we have received per week is 750 litres, DRC 28 %, (some variations were encountered during the wet season).

Concerning the chemicals, the only problem was with phenylhydrazine, finally the product was ordered at Hoechst Germany through its african subsidiary Hoechst-Ivoire. Help from UNDP was appreciated, especially for the customs operations. Six 200 litre drums arrived during the first week of April ; this amount allows a work programme of around 75 batches.

Safety data sheets were obtained with all the information concerning storage, handling and protective equipment to work safely. In addition a safety shower was installed near the pilot plant.

5.3.2. Reactions parameters

A pre-start audit was performed early in April, followed by a water-batch in order to have a smooth starting-up with people acquainted with the new technological environment.

A standard batch is designed to produce 200 kg of rubber from 750 litres of latex, for that we have respected the reactions parameters defined at Le Mans.

Phenylhydrazine is blended with water at 60° C to obtain an emulsion and added at the beginning of the reaction, in a single shot, when the stabilized latex is at the same temperature. Then we depolymerize on a continuous manner, day and night, during at least 24 hours.

Air bubbling is monitored by a needle valve, but this is certainly the most critical point concerning the reproducibility.

Coagulation is done in general with acetic acid (some experiments with formic acid did not give any difficulty) but lab-work has shown that we can reduce the amount from 20 litres of pure acid to 10 for 200 kg of dry rubber.

After washing, 3 times with water, the obtained coagulum is dried at 50° C-60° C under low pressure (150 mm Hg).

The details concerning mass and energy balance are given in tables 5.V., 5.VI. and 5.VII. for some "standard" batches.

Table 5.V.

Latex stabilization

Batch n°	P 285	P 385	P 485	P 585
Clone	GT 1	PB 86	PB 86	PB 86
Preservation (NH_3)	9.0 g/l	3.5 g/l	3.5 g/l	3.5 g/l
Maturation time	47 days	48 h	24 h	24 h
Stabilization : active material, based on dry rubber				
Nekal BX	1 %	1 %	1 %	1 %
Caustic	0.2 %	0.2 %	0.2 %	0.2 %
Energy required (kwh)	20	31	1	1
Time (agitation)	24 h	24 h	1 h	1 h
Temperature	25° C	25° C	25° C	25° C

Table 5.VI.

Depolymerization and coagulation

Batch n°	P 285	P 385	P 485	P 585
Depolymerization :				
- phenylhydrazine (l)	15.7	15.7	15.0	15.0
- water (l)	47	47	45	45
- total rubber content	200 kg	200 kg	190 kg	190 kg
- final DRC (%)	27.5	27.5	27.5	27.5
Temperature (° C) :				
- beginning	63	58	68	58
- after 4 hours	67	71	65	68
- end	67	65	65	65
Total reaction time (h) :	24	24	24	24
Energy required (kwh) :	225	154	160	176
Coagulation :				
- acetic acid at 50 %	40 l	40 l	40 l	40 l
- temperature (° C)	60	60	60	60
- time (h)	1	1	1	1
- energy (kwh)	7	8	8	6
- water collected (l)	415	417	346	360

Table 5.VII.

Washing, drying and global rate

Batch n°	P 285	P 385	P 485	P 585
Washing :				
1st washing				
. water in (1)	400	400	300	300
. water out (1)	330	352	185	170
2nd washing				
. water in (1)	300	200	200	200
. water out (1)	210	175	195	180
3rd washing				
. water in (1)	300	200	150	120
. water out (1)	285	205	155	120
Drying :				
- rubber temperature	58° C	60° C	55° C	55° C
- set point	100° C	100° C	120° C	120° C
- time (h)	16.0	17.5	11.5	13.0
- energy (kwh)	368	290	322	285
- water collected	non available	278 1	275 1	300 1
Global rate kwh/kg of rubber	2.90	2.25	2.36	2.27

The depolymerization results are given on figure 5.4. from where we can conclude that it is possible to produce, at semi-industrial stage, liquid rubber with a final molecular weight around 10,000 by using the standard rate of phenylhydrazine.

Waste water is produced by coagulation and washing, until now it was totally destroyed by incineration but this way is expensive. After several meetings with local authorities and water technical services, analyses were made in France and in Côte d'Ivoire to evaluate the possible toxicity before and after filtration on active black carbon. We are now allowed to evacuate the water, after filtration, in the lagoon due to its very low toxicity.

These productions were made in April and early in May 85. The 10th of May, an official ceremony of inauguration took place at Bimbresso with the presence of representants from Research Scientific Ministry of Côte d'Ivoire,international organizations (UNIDO, IRRDB), West Germany Embassy and local authorities. Performance tests were done (see table 5.VIII)and comparison with contract requirements shows that our production have reached the objectives.

Table 5.VIII.

Batches n°	P 285	P 385	P 485	P 585	Contract requirements
Initial DRC of latex %	33.3	34.3	30.2	30.3	30 - 45
Mechanical stability (s)	> 540	> 540	> 540	> 540	> 540
$\overline{Mv}$ (final product)	15 200	11 600	14 400	14 000	10 000 - 15 000
Volatile matters %	0.45	0.42	0.31	0.22	< 1
Nitrogen %	0.65	0.66	0.64	0.58	< 1.2

Specifications :

Liquid natural rubber is specified as a normal rubber.
The average values obtained over a long period of production are :

Nitrogen content	:	0.7 %
Ash content	:	0.4 %
Dirt	:	0.015 %
Volatile matters (after 3 hours at 100° C)	:	0.5 %.

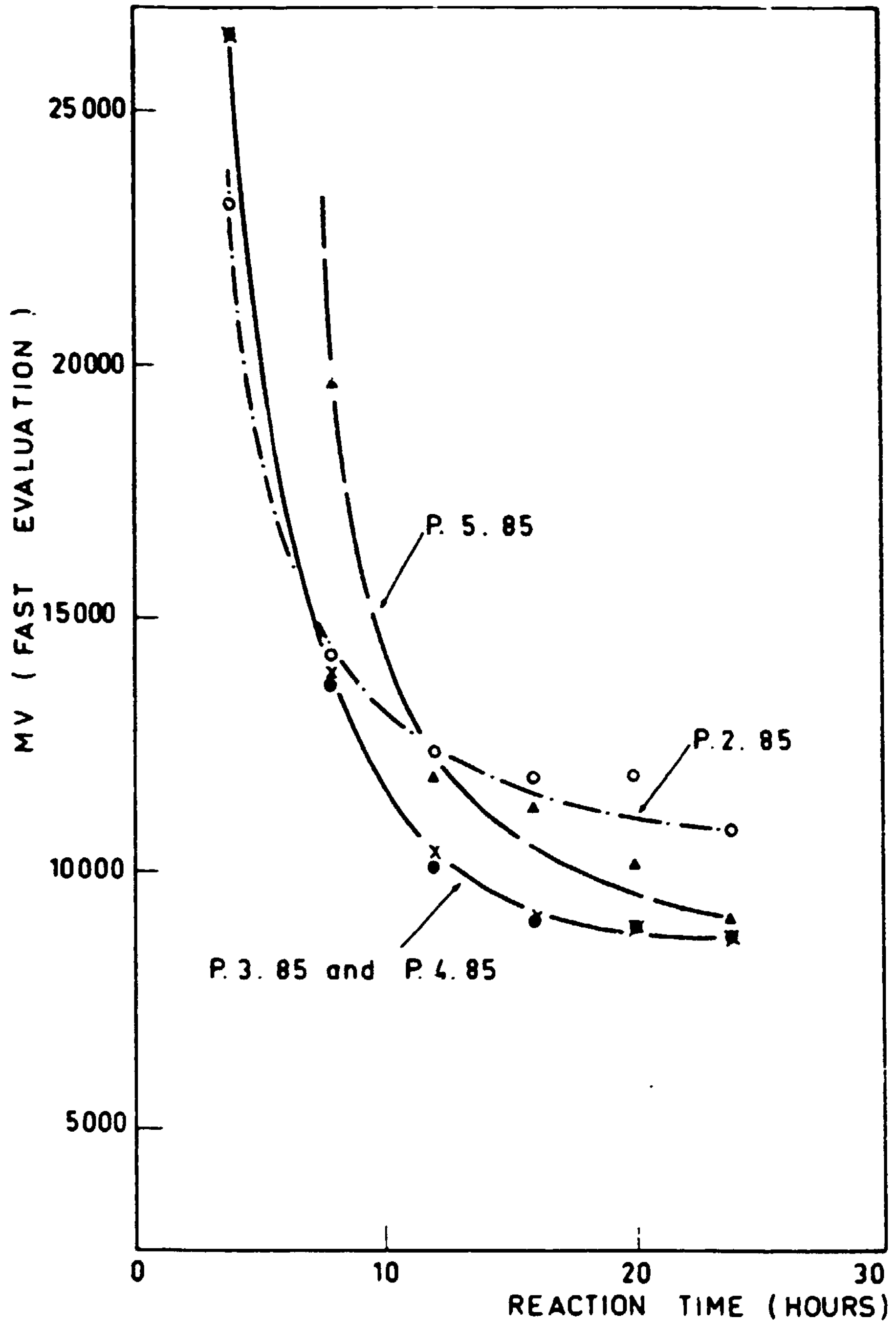


Figure 5.4. : Comparison of depolymerization reaction kinetics of the first trials

5.3.3. Reproducibility

As mentioned before, the critical point concerning reproducibility is monitoring air flow. Our equipment allows us to "control" air flow as a function of the time by opening the needle valve, but to know exactly the volume of air entering the reactor per minute, an accurate flow meter is missing. A thermodynamic calculation gives an estimation based on the compressor performances.

Four batches were made "in the same conditions". We will find the results of depolymerization kinetics and air flow in the figure 5.5. and the table 5.IX. Even with small variations concerning the actual air flow (especially at the beginning of the reaction) we obtained a good reproducibility because all the final molecular weights are within a range of 10,000 ± 10 %.

Table 5.IX.

Reaction time (hours)	Average air flow (l/min)			
	P 25	P 26	P 27	P 29
1	46	39	42	52
2	44	36	44	60
3	57	44	52	58
4	57	50	57	55
5	54	66	49	69
6	52	68	41	74
7	58	61	44	66
8	61	68	58	74
9	69	68	77	77
10	71	79	77	80
12	71	80	81	86
14	87	70	85	88
16	89	82	89	69
18	90	81	85	88
20	91	77	86	93
22	95	86	83	84
24	70	82	92	88
26	41	88	96	115
28	81	101		
Average over the all reaction time	71.4	73.8	74.5	79.0

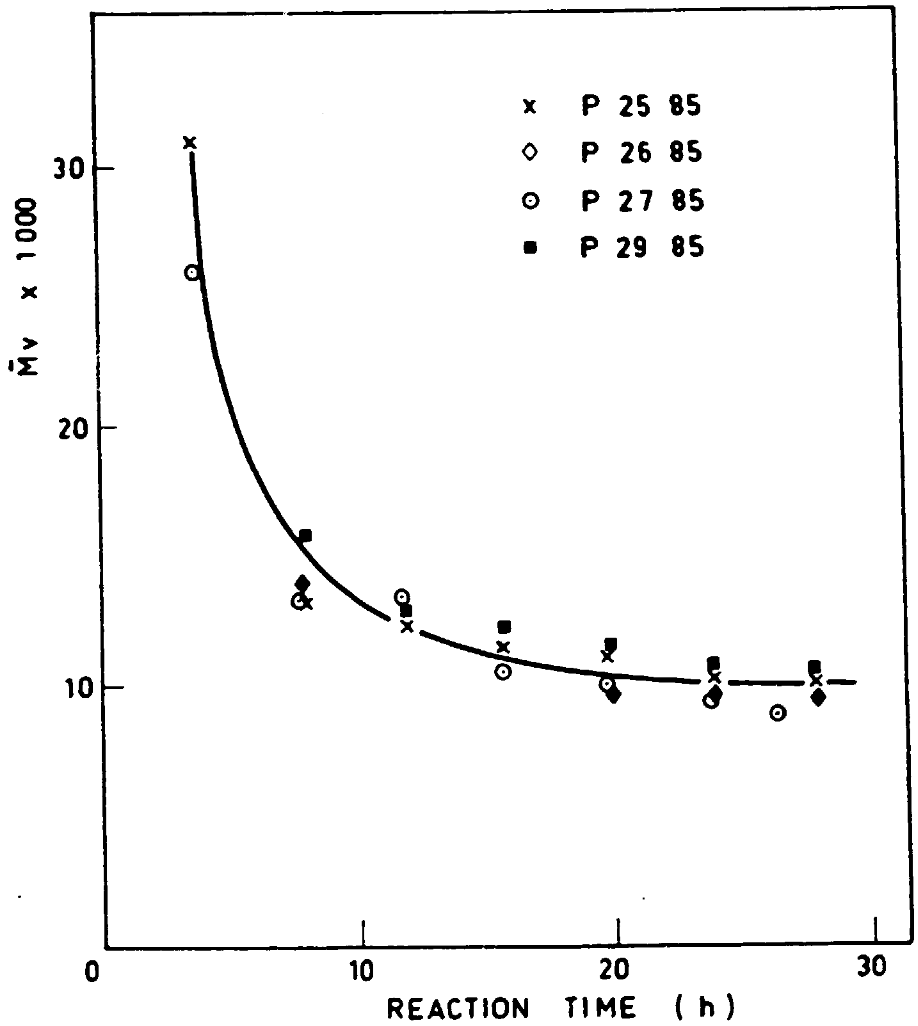


Fig. 5.5. Depolymerization kinetics

5.3.4. Obtention of low molecular weight

In order to obtain liquid rubber with very low molecular weight (< 8000), we have produced 3 batches by using different rates of phenylhydrazine as indicated in table 5.X.

As we can see on figure 5.6., there is a little dispersion between P 12 85 and P 14 85 but, and maybe this is more important, increasing the level of phenylhydrazine by 50 % does not give any advantage. It seems that there is a limit : we cannot obtain a depolymerized rubber with a molecular weight (viscometric value) below 6000, at least with this process.

Table 5.X.

Batch n°	Rate of phenylhydrazine	$\overline{M}$v (end of depolymerization
P 9 85	standard + 50 %	6 500
P 12 85	standard + 25 %	6 040
P 14 85	standard + 25 %	7 350

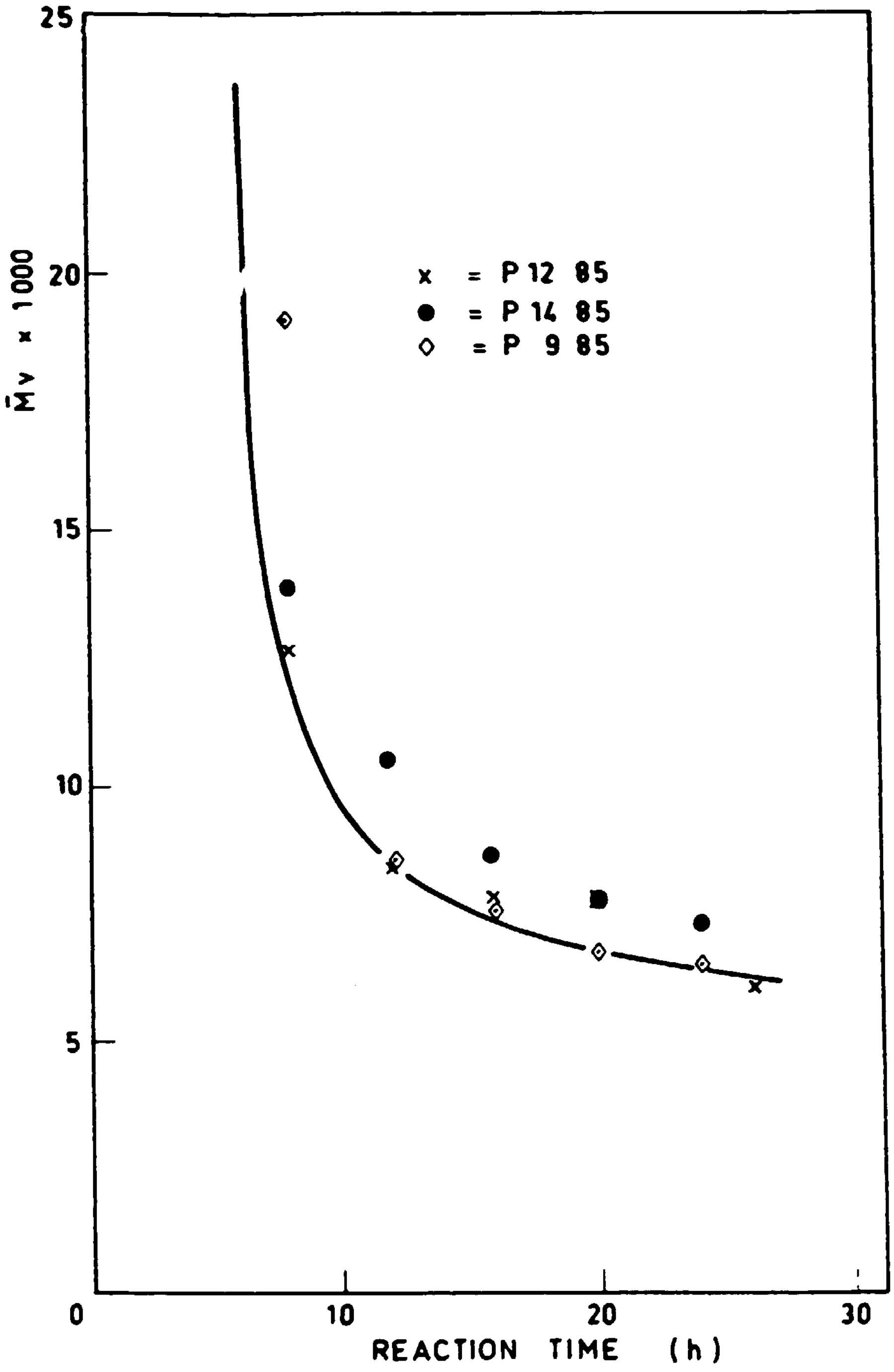


Fig. 5.6. Depolymerization kinetics
low molecular weight obtention

5.3.5. Obtention of high molecular weight

To produce liquid rubber with "high" molecular weight (around 20,000), we have reduced the level of phenylhydrazine. The first batch (P 15 85) was made with only 25 % of the standard amount. Effectively at the end of the depolymerization the molecular weight was 21,500, but after coagulation it was quite impossible to evacuate the water due to the coagulum high viscosity. Washing was only partially done and drying was long. The final product -after certainly a lot of side reactions- had a molecular weight above 40,000.

For the next productions we used 50 % of the standard level of phenylhydrazine. Molecular weight was measured at different stages of the process and all the results are in table 5.XI. The final results are within the range : 20,000 ± 22 %, but the main conclusions concern the dispersion of the results, more important after drying than at the end of depolymerization, and the large augmentation of molecular weight during the process. This point will be explained later on.

Table 5.XI.

Batch n°	P 16 85	P 17 85	P 18 85	P 19 85
End of depolymerization	12 600	13 650	15 050	13 200
After coagulation	15 900	15 950	19 100	12 500
Before drying	15 600	17 300	19 250	12 400
After drying	20 000	18 600	24 450	17 300

Molecular weight at different stages of the process.

5.3.6. Reactions under pressure

Depolymerization reaction takes place in liquid phase and oxygen plays an important role ; it was envisaged to increase the amount of dissolved oxygen in water by increasing the reaction pressure. Our aim was to improve the kinetics of reaction to allow a faster reaction or to use less phenylhydrazine.

Two batches were made (P 2285 and P 2385) at 1 bar above atmospheric pressure and one (P 2485) under 2 bars. The results of the depolymerization are given in the figure 5.7. and indications of air flow in the figure 5.8.

P 2385 was done with the maximum possible air flow we can have with the existing equipment and we cannot see any improvement concerning the obtained molecular weight. For P 2485 (under 2 bars), the air flow was even less important due to a greater "resistance" from the reactor. In conclusion it seems that there is no immediate advantage to depolymerize under pressure, because it was not possible to obtain a molecular weight below 10,000 with the standard level of phenylhydrazine.

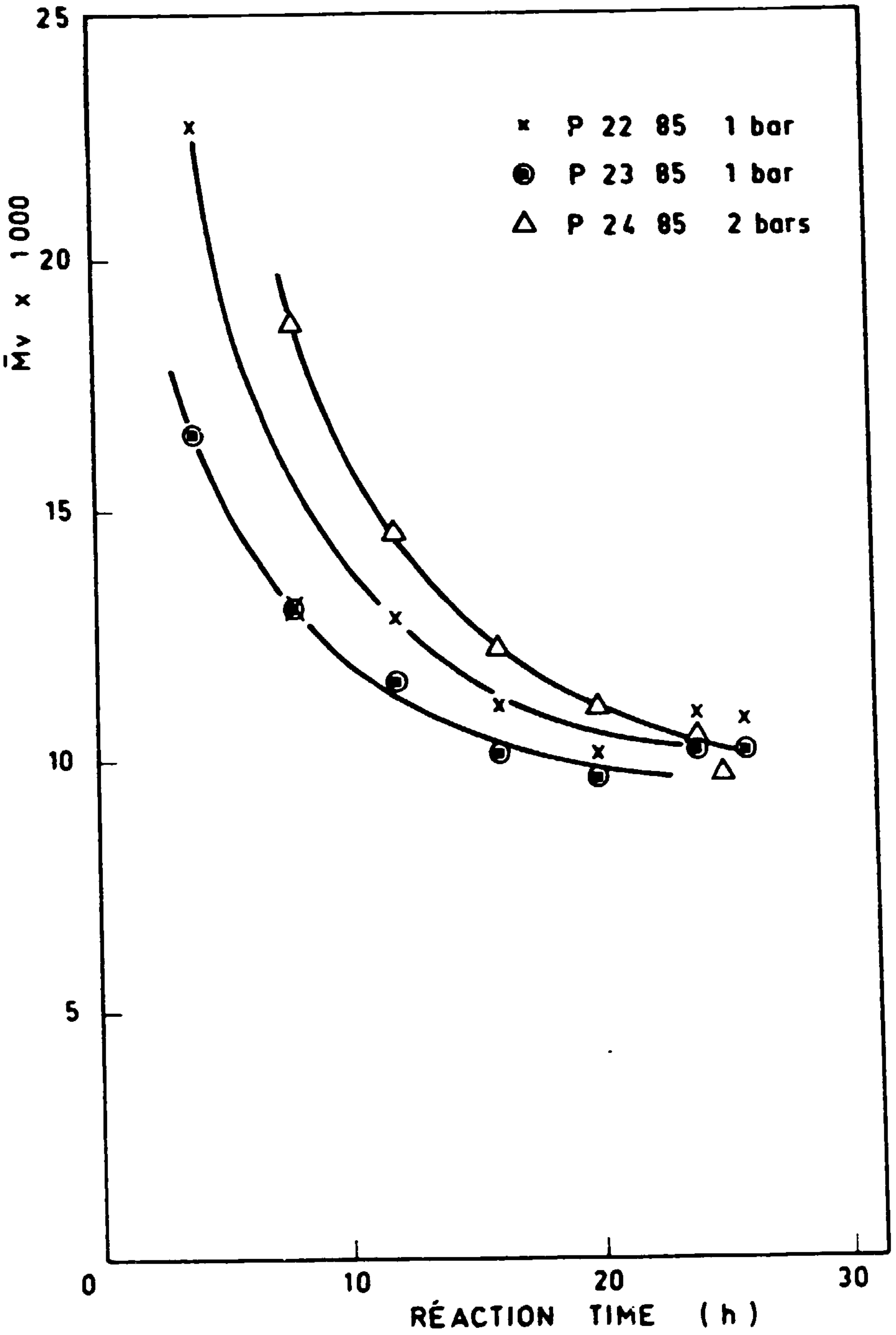


Fig. 5.7. Depolymerization kinetics under pressure

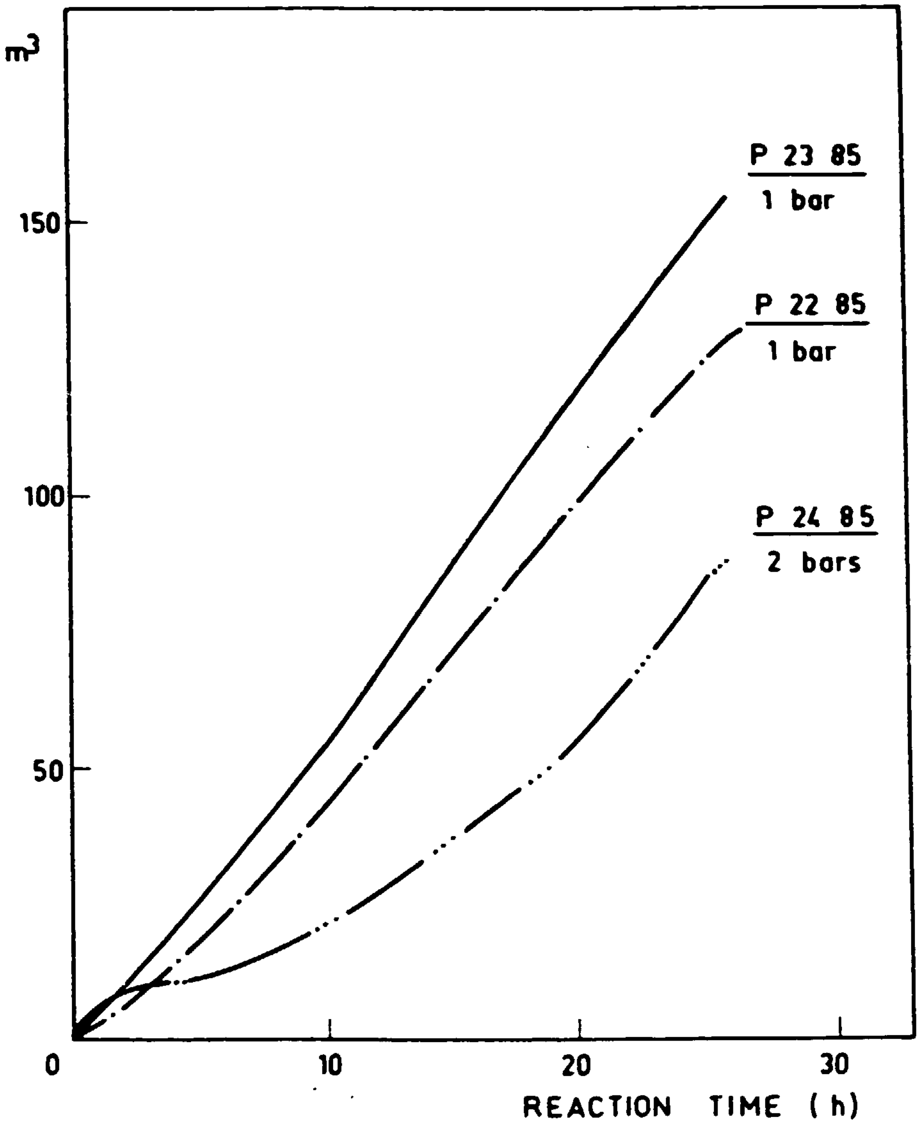


Fig. 5.8. Air Flow/Reaction time

5.3.7. Drying

As seen before, we generally obtained an increase of the molecular weight during the second part of the process, that means after depolymerization. In addition, ageing study has shown that Brookfield viscosity of our production increases with the time. These phenomena have never been observed in the laboratory (in France and in Côte d'Ivoire.

The main difference between lab-scale and pilot plant is the ratio : external surface of the product/mass of the product. Now this parameter is a key-factor controlling heat transfer (to warm-up during drying or to cool-down before coagulation and washing).

We, first, have studied the influence of the drying step. In our case (pilot plant) in order to have a relatively fast operation, we have fixed the temperature set point of the reactor jacket at 120° C, and that may cause some chemical modifications in the rubber structure.

Several batches were produced varying the temperature set point as indicated in table 5.XII.; in figure 5.9. the behaviour of two of them is indicated : there is no improvement in stability by decreasing the temperature set point during drying.

5.3.8. Coagulation study : influence on Brookfield viscosity and ageing/stability

In this paragraph we have studied the influence of coagulation temperature and period on the final rubber Brookfield viscosity and stability versus time.

Depolymerized latex was cooled-down to about 40° C and coagulation was made as fast as possible. The obtained coagulum was washed three times, as usually, and dried (set point at 90/85 or 120° C). In all cases (see table 5.XIII. and figure 5.10.) the Brookfield viscosity of the dry rubber is constant over a period of now six weeks, in contrast with the results obtained by "hot temperature" coagulation.

If the future results confirm this trend, the explanation of the phenomenon should be found in the coagulation chemistry. One possible mechanism is the following : addition of acid allows hydrolyse of end groups and forms carbonyl functions giving the possibility for polyamines to develop crosslinking reactions.

BATCH N°	COAGULATION		DRYING			MOLECULAR WEIGHT (viscometric)			BROOKFIELD VISCOSITY
	Temperature (° C)	Period (min)	Set point (° C)	Period	Total	After coagulation	Before drying	After drying	Trend after 6 weeks
P 21	62	105	120	10 h 30	10 h 30	8 450	8 450	10 500	↗
P 22	62	65	90	19 h	19 h	11 000	9 600	12 800	↗
P 23	60	135	90 85	14 h 45 6 h 15	21 h	8 900	8 600	10 000	↗
P 24	69	85	90 85	15 h 45 2 h 45	18 h 30	8 200	9 130	10 750	↗
P 25	60	100	90 85	13 h 15 2 h 15	15 h 30	-	10 000	11 450	↗

Table 5.XII.

Influence of drying temperature on
molecular weight and Brookfield stability

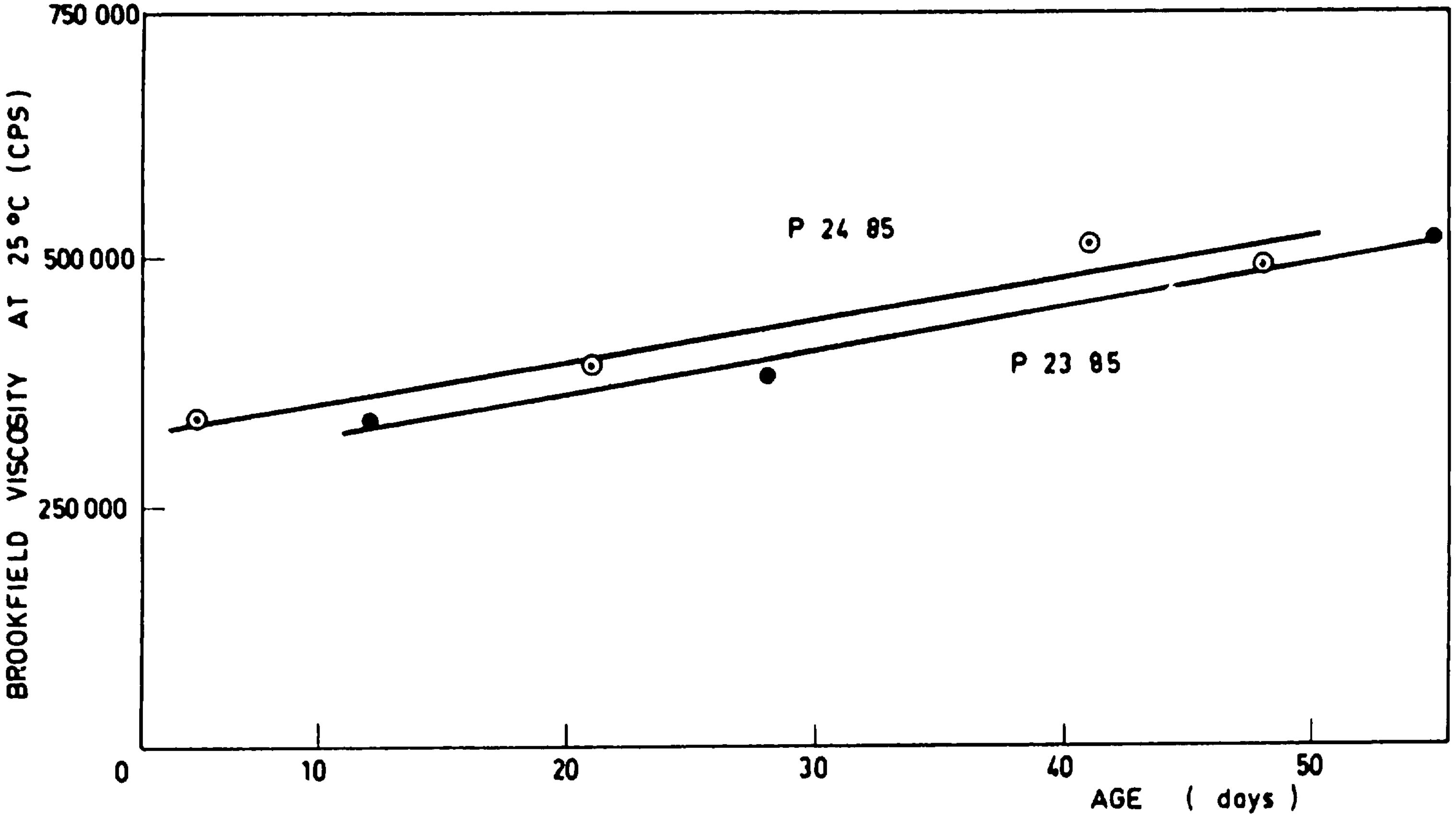


Fig. 5.9. Storage evolution of LNR viscosity
with 60°C coagulation temperature

BATCH N°	COAGULATION		DRYING			MOLECULAR WEIGHT (viscometric)			BROOKFIELD VISCOSITY
	Temperature (° C)	Period (min)	Set point (° C)	Period	Total	After coagulation	Before drying	After drying	Trend after 6 weeks
P 26	42	90	90 85	13 h 30 1 h 30	15 h	9 960	9 900	11 150	→
P 27	40	20	90 85	11 h 30 1 h 30	13 h	8 820	9 380	10 500	→
P 28	40	25	120	9 h 15	9 h 15	10 275	9 450	11 200	→

Table 5.XIII.

Influence of coagulation on Brookfield stability

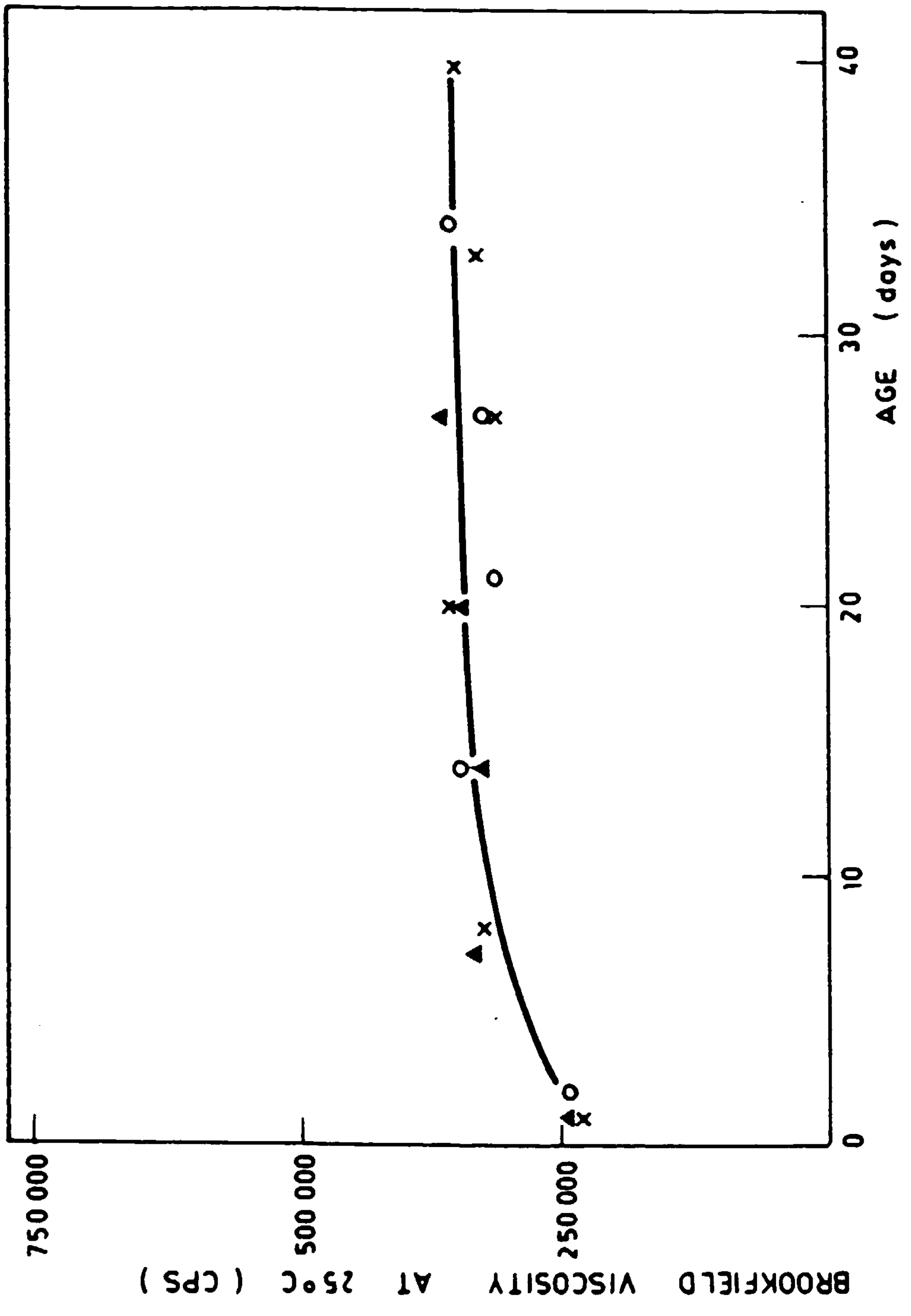


Fig. 5.10. Storage evolution of LNR viscosity with 40°C coagulation temperature

CHAPTER - 6

CHEMICAL MODIFICATIONS OF LIQUID NATURAL RUBBER

6.1. CHLORINATION

6.1.1. Chlorination of high molecular weight natural rubber

As far back as the end of the 19th century, chlorination of high molecular weight natural rubber has been studied many times. Among the possible methods of chlorination, only the action of gaseous chlorine on rubber in solution has led to a method of chlorinated rubber preparation at the industrial stage. Owing to its low solubility, natural rubber must be degraded before and during chlorination. This degradation is obtained mechanically and chemically using heavy and costly equipment. So, prolonged action of chlorine on rubber in solution at around 5 % in an inert solvent such as carbon tetrachloride gives a hard, pulverulent and whitish material possessing no more elastomeric property. Chlorine rate in weight is around 65 %.

Thanks to a sum of particularly interesting properties, chlorinated rubber find applications mainly in the paint industry and also in the adhesive and ink industries. Chlorinated rubber gives excellent anti-corrosive properties to paints and good protection in industrial and marine environments. Besides, incorporating chlorinated rubber into some solvent-adhesives facilitates adhesion on certain substrats.

However, as to meet users' requirements, chlorinated rubber producers have been, for the last ten years, increasingly directing towards chlorination of synthetic polymers to the detriment of natural rubber : these polymers have lower and well-controlled molecular weights, making it possible to obtain chlorinated products whose viscosities in solution are better defined.

Chlorination of depolymerized natural rubber of low and well-defined molecular weight can allow natural rubber to reconquer a market it has partly lost, especially in the countries producing both gaseous chlorine and natural rubber.

6.1.2. Chlorination of liquid natural rubber in solvent phase

According to the litterature, a certain number of parameters affect the chlorination reaction of polyisoprenes, making the chlorine content of the final product vary.The objective therefore was to define an operating method capable of giving, with LNR, chlorinated rubber of a fixed chlorine content close to that of commercial chlorinated rubber (around 65-68 %). It is known that the fixed chlorine content on polyisoprenes must reach this value for final polymer to have a good stability.

6.1.2.1. Development of the operating method

Every chlorination reaction has been carried out with a one-litre reactor fitted with one agitator, one cooler, one thermometer and one plunging tube with a fritted end allowing either chlorine or chlorine-gas diluting mix to diffuse. Above, a flow-meter controls the chlorine flow (0 to 530 ml/mn) and below, a soda-trap collects excessive chlorine and hydrochloric acid formed during the reaction.

Carbon tetrachloride, totally inert towards chlorine, is used as solvent. In general, solution concentration equals 8 %, i.e. 40 grams of LNR dissolved into 500 ml of carbon tetrachloride. The reactions have been performed with various temperatures and durations. It is important to note that, whatever operating method is selected, the first chlorination phase is an exothermal and highly chlorine-consuming reaction while the following phases are much slower. During the reaction, chlorine flow is adjusted to avoid excessive loss. Having the reaction lasted 6 to 8 hours, chlorine flow is stopped and reaction continues during about 17 hours (one night) with chlorine dissolved in the reactional medium. After degassing at the end of the reaction, chlorinated rubber is collected by solvent flash distillation, ground and dried in a ventilated oven at 70° C during 48 hours.

Chlorine content is obtained by silver nitrate determination after mineralization by the Wickbold's system.

First, the study shows that, whatever the operating conditions are, without catalyzer and at atmospheric pressure, chlorination of natural liquid rubber leads to a polymer with a chlorine content below 60 %. The most significant results of this study are shown in table 6.I. Studying the influence of catalyzers during chlorination has shown that only the supply of ultra-violet rays can markedly increase the chlorine content measured (71 %). It should however be mentioned that this chlorine content value does not correspond exactly to the chlorine content really fixed on polymer ; it is known that, as in the case of commercial polymers, total elimination of carbon tetrachloride during drying is impossible.

Second, the study of the effect of U-V irradiation has been particularly detailed. The generally admitted chlorination mechanism of 1-4 CIS polyisoprenic structures, of which no one is really sure, is represented by figure 6.1. It is based on three main phases : the first one corresponds to a rapid substitution reaction, the second

Table 6.I

CHLORINATION OF LIQUID NATURAL RUBBER

Sample	$\bar{M}v$ (NRD)	Concentration (g/100 ml)	Chlorine flow (ml/mn)	Diluent gas	Catalyst	Temperature (°C)	Time (hours)	Chlorine content (%)
NRDC 1	22,000	8	370/120 (a)	-	-	30 - 35	6	54
NRDC 2	22,000	8	370/120	-	-	30 - 35	6 + 17(b)	60
NRDC 2 bis	11,400	8	380/150	-	-	30 - 35	6 + 17	59
NRDC 3 (c)	14,000	8	380/150	-	-	30 - 35	6 + 17	58
NRDC 4	22,000	9	380/150	Nitrogen	-	30 - 35	8 + 15	57
NRDC 5	22,000	9	380/150	Nitrogen	-	60 - 68	6 + 17	58
NRDC 6	22,000	8	150	Nitrogen	-	30 - 35	8 + 15	58
NRDC 7	22,000	8	150	Nitrogen	Iodine (1 %)	30 - 35	8 + 15	56
NRDC 8	22,000	8	380/150	-	-	30 - 35	6.5 + 17	61
NRDC 9	22,000	8	380/150	Oxygen	Oxygen	30 - 35	7 + 17	59
NRDC 10	22,000	8	380/150	-	U.V. light	30 - 35	6.5 + 17	71
NRDC 11	11,400	8	380/150	-	U.V. light	30 - 35	6.5 + 17	71
IRC 1 (d)	15,000	8	380/150	-	-	30 - 35	6.5 + 17	65

a) 370 ml/mn during the first two hours, 120 ml/mn after.

b) During 17 hours, chlorine flow is stopped.

c) From field latex.

d) Synthetic polyisoprene 1-4 cis.

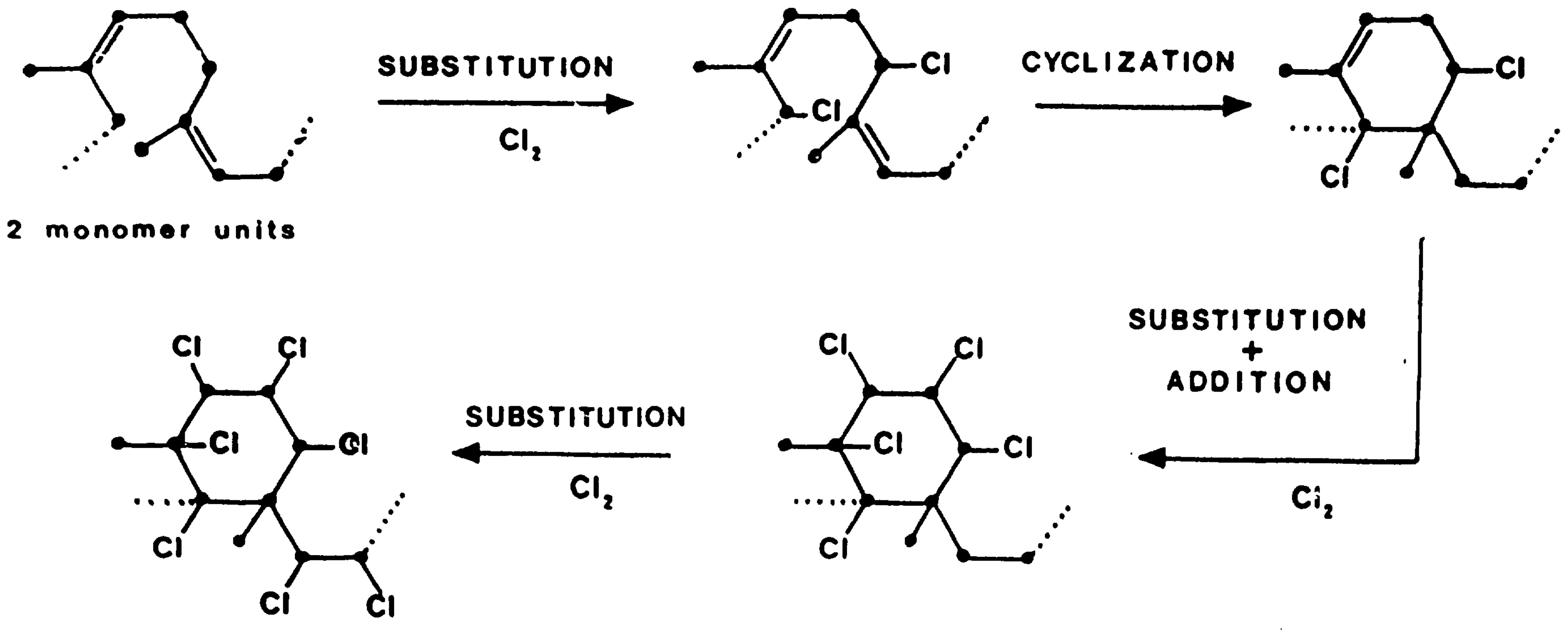


Figure 6.1

CHLORINATION MECHANISM OF POLYISOPRENE

to three slower reactions superposed (cyclization-addition-substitution) and the third to a last slow reaction of substitution. It has been showed that the effect of U.V.catalysis is maximal in the second phase of the reaction ; in accordance with what is described in the litterature, U.V.irradiation promotes addition reaction to the detriment of cyclization reaction, which is carbon-carbon double bonds consuming and decreases the possibility of chlorine fixation.

But it is obvious that the duration of each phase cannot be accurately determined. That is why it is preferable to maintain U.V. catalysis throughout chlorination.

The operating method has been developed on liquid rubber derived from centrifuged latex. Using LNR originated from field latex gives chlorinated rubber having more or less the same properties.

6.1.2.2. Physico-chemical properties of chlorinated LNR

The main physico-chemical properties of chlorinated rubber have been compared with those of commercial rubber such as Alloprene R 40 and R 10 from I.C.I.and Parlon S 125 from Hercules.

. Colour : chlorinated LNR are slightly more yellowish than the commercial products.

. Solubility : chlorinated LNR are perfectly soluble in the conventional solvents of chlorinated rubber (aromatic, chlorinated, esters...).

. Chemical structure : the Infrared and Proton Nuclear Magnetic Resonance (NMR) spectrograms of chlorinated LNR are comparable to those of the commercial products. However, NMR shows, for chlorinated LNR only, the presence of ethylenic protons corresponding to residual carbon-carbon double bonds ; this has been confirmed through double bonds determination by catalytic hydrogenation. High chlorine content therefore could be explained by the fixation of CCL3 radicals, resulting from the photochemical fission of carbon tetrachloride.

. Residual carbon tetrachloride (CCL4)

A method of quantitative analysis of residual CCL4 in chlorinated rubber has been developed : it is an adaptation of the method used by I.C.I. ; it is based on detection by liquid gas chromatography. For instance 10 to 12 % in weight of residual CCL4 have been measured in a chlorinated LNR recovered in a conventional way and containing 71 % chlorine : consequently, the chlorine content really fixed on polymer is only around 65 %. As such a high residual CCL4 content cannot be accepted owing to the legislations in force, the recovery process has been modified. An ICI patented method consists in adding to the chlorinated rubber solution, at the end of chlorination and before flash distillation, a lubricant of the glyceride type. Various products have been tried :

stearic acid, epoxydated soya oil, glyceral monostearate and ethyl palmitate ; the latter gives the best results. With 5 % in weight of ethyl palmitate as compared to chlorinated LNR, the CCL4 content is decreased to 0,5 %. It is 4,3 % with 5 % of epoxydated soya oil, which, present in the final product, can play, thanks to its epoxy group, a role of stabilization agent towards dechlorhydration.

. Viscosity in solution

Commercial chlorinated rubbers are usually classified in various grades (5, 10, 20, 40, 90 and 125) which correspond to the viscosities of polymer in solution. Alloprene R10, in solution at 20 % in weight in toluene, leads to viscosity at 25° C of around 10 centipoises. Viscosity of liquid natural rubber with a molecular weight from 10,000 to 20,000 and chlorinated by U.V. catalysis, ranges from 5 to 10 centipoises. Various chlorination tests with different LNR initial concentrations (8, 10, 12 and 14 %) did not give any considerable variation in viscosity. On the other hand, it is very interesting to note that chlorinated LNR can be prepared by substantially decreasing the amount of solvent used.

As viscosity of a chlorinated LNR, prepared with rubber of a molecular weight equalling 50,000 is not higher, it should be admitted that U.V. irradiation continues polymer depolymerization during chlorination.

. Thermal stability

A study by nitrogen thermogravimetry has shown that thermal stability of maximally chlorinated LNR was close to that of Alloprene : the first weight losses are observed around 129-130° C. On the other hand, the method by Rosenthal and Schulze shows a very large difference in behaviour between commercial products and chlorinated LNR ; this very sensitive method determines the ability of chlorinated rubber in solution to release hydrochloric acid at 100° C. This ability is close to one hour in the best case for chlorinated LNR while it is around 12 hours for the commercial product.

6.1.3. Chlorination in latex phase

With a deep modification in operating conditions, chlorination of natural rubber can be achieved in latex phase. This has been investigated many times in the past. But no method of chlorination in latex phase could really approach the industrial stage. The chlorinated rubbers obtained are generally insufficiently modified, unstable and insoluble.

As depolymerization of natural rubber in latex phase can lead to a varied range of molecular weights, it seemed relevant to perform a few orientation tests on LNR latex chlorination.

In both latex and solvent phases, the action of chlorine on polyisoprene releases hydrochloric acid, it therefore is indispensable to replace the ionic stabilizer by a non-ionic stabilizer before the depolymerization reaction. Besides, latex has to be highly acidified before chlorination to avoid the fixation of hypochlorous acid. On latex from more or less depolymerized rubber whose serum normality has been brought to around 6 N, various chlorination reactions have been carried out, making some parameters vary : duration, temperature, U.V. catalysis. In the best case, chlorinated rubber contains a maximum of 60 % of chlorine and polymer becomes insoluble and unstable with time owing to the insolubility of the product, additional chlorination in solvent phase is made difficult.

6.1.4. Conclusion

This study shows that liquid natural rubber can be used as original product to obtain chlorinated rubber with properties comparable to those of the commercial products. However, the few differences in structure and behaviour are probably due to the chlorination method adopted which uses U.V. radiations.

The bibliographical data related to the industrial process are few : they seem to imply that at least one phase of the chlorination reaction is carried out under pressure, which should make it possible to reach the maximum chlorine content desired. Although the equipment required is much more sophisticated and expensive, the study of LNR chlorination under pressure is worth undertaking.

6.2. MODIFICATION WITH MALEIC ANHYDRID

6.2.1. Review

Fixation of maleic anhydrid on high molecular weight natural rubber was thoroughly studied by the Institut Français du Caoutchouc around twenty years ago ; the aim was to improve various properties of vulcanized elastomer such as increase in modulus and resistance to repeated bending.

This study has emphasized two possible mechanisms of maleic anhydrid fixation on one polyisoprenic structure :

- the first is of the radical type ; it is induced by moderate temperature heating in presence of free radical catalysers,

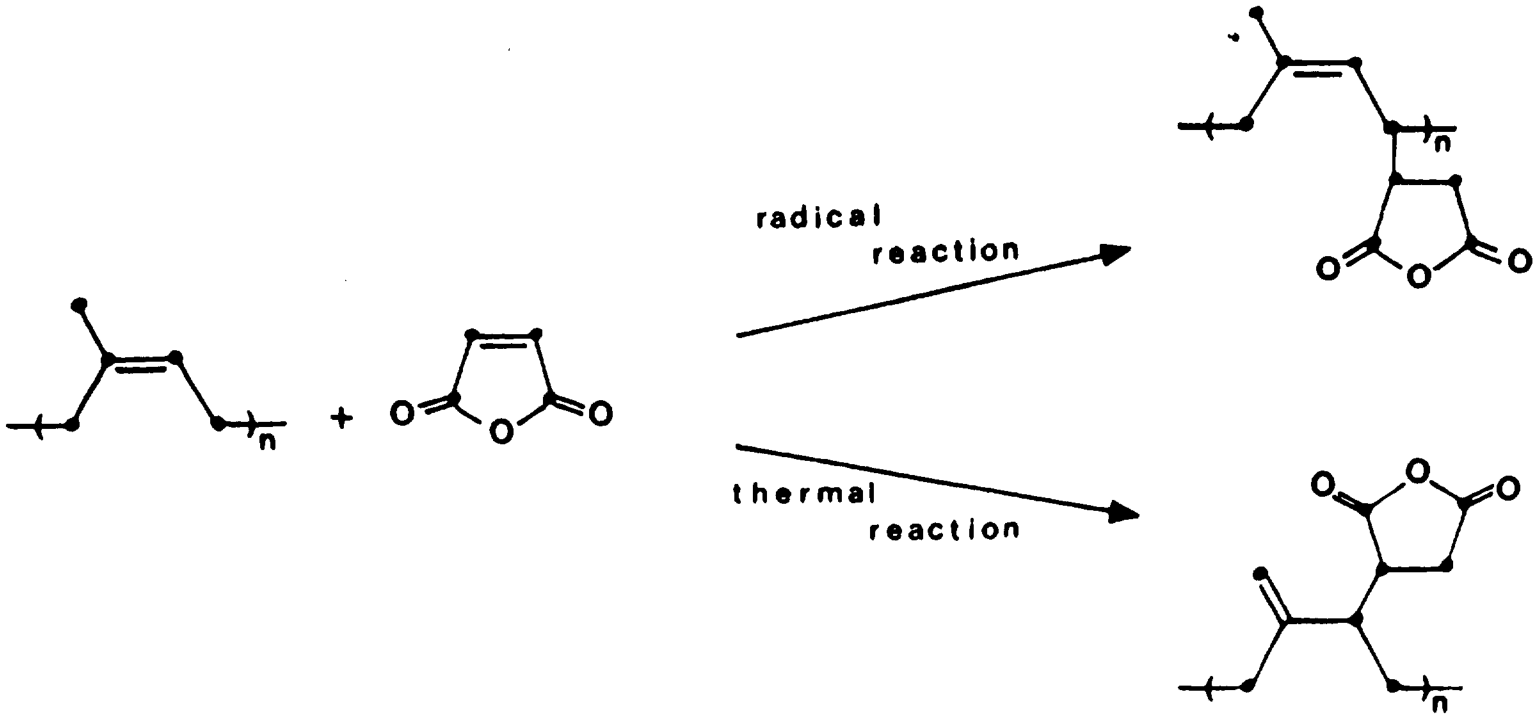
- the second is of the thermal type ; it is induced by high temperature heating without any catalyser.

As shown by figure 6.2., the radical mechanism involves a substitution reaction on methylene - α - group of double bond while the thermal mechanism is a "ène-reaction"involving electronic transfers. The works described below confirm that both fixation mechanisms are possible on low molecular weight natural rubber.

The modification of liquid natural rubber primarily aims at improving adhesive properties of polymer especially on polar substrates and metals. Beforehand a few promising orientation tests had confirmed this hypothesis.

Figure 6.2

ADDITION OF MALEIC ANHYDRID TO POLYISOPRENE 1-4 CIS



6.2.2. Radical fixation of maleic anhydrid

6.2.2.1. Effect of reactional parameters

The effectiveness of the reaction of maleic anhydrid radical fixation on liquid rubber can be affected by the following parameters :

- type of LNR
- type of solvent
- type and amount of radical initiator
- initial LNR content
- initial maleic acid/polyisoprene unit molar ratio
- reaction temperature and duration.

At the end of the reaction, modified polymer is recovered by precipitation followed by dissolution and precipitation again to remove non-fixed maleic anhydrid. After polymer drying, the oxygen content obtained by elementary analysis gives the modification rate.

A first test series made it possible to compare for this reaction the effectiveness of three radical initiators of different structures. Azobisisobutyronitrile and paramenthane hydroperoxyde give more or less identical modification rates, while benzoyl peroxide is less effective. The amount of initiator used is 3 % in weight as compared with LNR.

With no variation in the other operating conditions, the modification rate decreases with the purification level of the solvent used but is not substantially modified, being the initial LNR derived from either centrifuged latex or field latex. The molecular weights of the LNR used are around 11,000.

For maleic anhydrid/LNR molar ratios ranging from 0.2 to 0.5, the fixation rate is proportionate to the initial reagent amount.

Maximal reaction temperature is 130° C and duration 5 hours. Increasing reaction time does not improve modification rate : the radical initiator therefore is totally consumed during this period of time.

In a range of 50 to 200 g of LNR per litre of solvent (xylene), initial polymer content has no effect on modification rate. It is noted that the very high solubility of low molecular weight rubber makes it possible to work on fairly high contents (20 %) ; beyond, reticulation may be feared.

In the best case however, the modification rate was only 13 % in weight of maleic anhydrid, that is about 11 % of modified isoprenic structures, with a rate of the fixation reaction below 40 %. This low rate is the reason why radical modification was later abandoned for thermal modification.

6.2.2.2. Analysis of modified LNR

In accordance with the mechanism supposed, Infra Red spectroscopy of maleic anhydrid radically modified LNR shows that the double carbon-carbon bond of 1-4 CIS polyisoprene is not disrupted. In addition to the signals characteristic of the anhydrid group, the presence of signals characteristic of the acid group is observed ; this is due to the opening of the anhydrid cycle which can be caused during reaction or during polymer recovery operations.

Besides, while modified polymer is perfectly soluble at the end of the reaction, it becomes hard, brittle and partly insoluble after solvent elimination. This phenomenon is probably caused by the formation of "hydrogen bonds" due to the presence of the free electronic doublets belonging to the oxygen atoms of the anhydrid and acid structures, being these bonds capable of forming a bridge between the polyisoprenic chains.

6.2.3. Thermal fixation of maleic anhydrid

6.2.3.1. Effect of reactional parameters

As thermal modification occurs in a very high temperature range (180 to 240° C), every reaction has been carried out in a 200 ml capacity autoclave. Most tests have been conducted using an initial LNR content of 20 % with xylene as solvent. An agent such as thrichlorotriazine or copper acetylacetonate is added to the solution at the rate of 0.1 % in weight as compared to LNR to avoid gel formation during the reaction. The influence of the various reactional parameters has only been studied on LNR derived from centrifuged latex.

With modified LNR recovery and analysis methods identical to those used in radical modification, the first test series has allowed the following conclusions to be drawn :

- between 180 and 230° C, modification rate is proportional to temperature, beyond, considerable decarboxylation reactions disturb the reaction,

- the presence of neutral atmosphere, nitrogen for instance, is not indispensable,

- the modification rate is proportional to the maleic anhydrid/LNR molar ratio and to reaction duration ; but when reaction exceeds 8 hours, no increase in the modification rate is observed.

As in the case of radical modification, the analysis of modified LNR shows a partial opening of the anhydrid cycles. It has been realized that this non-controlled opening altered the method of calculating the modification rate ; in some cases, this error can be considerable. The observations made us modify the techniques of polymer recovery and analysis for the continuation of the study.

As far as polymer recovery is concerned, the precipitation solvent is not methanol anymore but ethanol, which is less reactive towards the anhydrid cycle ; the duration of contact with ethanol is reduced to a minimum and addition of toluene-petroleum ether makes it possible to eliminate residual ethanol. Modified LNR is kept in solution in a toluene-methyl ethyl ketone.

The fixation rate therefore is measured by simultaneous determination of the anhydrid and acid groups by tetrabutylammonium hydroxyde : it is expressed in number of modified structures.

Under these conditions, a check reaction of a synthetic polyisoprene modification occurs without anhydrid cycles opening. This opening therefore is linked to the very nature of LNR.

A whole series of modified polymers has been prepared, making the maleic anhydrid/LNR molar ratio vary. The modification rate ranged from 1.7 to 32.7 %. When reaction is carried out during 8 hours at 225° C, fixation rate is around 65 %.

6.2.3.2. Analysis of modified LNR

Contrary to the observations made on radically modified LNR, the Infra Red spectroscopic study of thermally modified LNR shows that the 1-4 CIS polyisoprene carbon-carbon double bond is slightly disturbed and that "exo" double bonds appear, in accordance with the mechanism proposed. When dry, modified LNR have the same properties as those described in the chapter concerning radical modification.

6.2.4. Estimate of the adhesive power of maleic anhydrid modified LNR

As LNR have to be kept in solution, they have been tested as solvent-adhesives to prepare two types of associations : aluminium/ aluminium and wood/wood.

The tests have been carried out as follows :

- modified LNR is put as solution at 50 % of dry extract on the two surfaces to paste, which have before been submitted to a specific surface treatment.

Having solvent been eliminated during half an hour at 60° C, both surfaces are brought into contact under slight pressure during one hour at 100° C. Shearing strengths are measured thanks to an electronic dynamometer with a 10 mm/mn traction speed.

As far as wood/wood associations are concerned, for a modification rate of 12 % (12 monomer units modified out of 100), the value of shearing strength exceeds that obtained with a polychloroprene-based check contact-adhesive (18.6 against 11.6 da N/cm2). When modification rate is 18 %, the break is not adhesive anymore but cohesive (the wood breaks).

For aluminium/aluminium associations, the most significant results have been grouped in table 6.II. They show that shearing strength reaches a maximum for a modification rate around 20 %. The maximal value obtained, around 110 daN cm2, is interesting ; it is however nearly half below that obtained with a commercial structural adhesive of the epoxy type.

Studying the formulation optimization and the operating conditions did not bring any significant improvement. For instance, adding in the solution of modified LNR, reticulating agents of various types (peroxyde, metallic oxide, dial, diamine) is on the whole detrimental to adhesive performances. Besides, the curing conditions corresponding to 60 minutes at 100° C or 10 minutes at 120° C are the most appropriate.

As to try to avoid the use of solvent, tests to prepare film adhesives have been carried out with LNR modified at 20 %. The film is made with the solution by solvent evaporation and placed between the two surfaces to paste. Shearing strength decreases by almost 50 % and film ageing is unsatisfactory.

Ultimately, storing a solution of LNR modified at 20 % during 2 months makes shearing strength decrease by about 25 %.

6.2.5. Extrapolation with field latex derived LNR

When the reaction of thermal maleic anhydrid fixation is applied to field latex derived LNR, the results obtained are markedly modified. During the reaction, a substantial increase in pressure is noted, probably due to the presence of carbon dioxide resulting from a decarboxylation much higher than that observed in a reaction on centrifuged latex derived LNR. It should therefore be admitted that the non rubber substances present in this LNR catalyse the decarboxylation reaction. This causes a sharp decrease in modification rates originating necessarily a drop in adhesive properties. This extrapolation could not be continued, through lack of time.

6.2.6. Conclusion

This study shows that maleic anhydrid modification of centrifuged latex derived LNR can be achieved under fairly simple operating conditions. For a modification rate of about 20 %, modified rubber possesses interesting adhesive properties which are comparable to those of certain structural adhesives. However, the operating conditions and especially the need to use a solvent may hinder the development of such a product.

On the opposite, the presence of reactive sites such as succinic anhydrid cycles makes it possible to envisage the fixation of active substances giving access to products with a higher value added.

Table 6.11

EFFECT OF MODIFICATION RATIO ON ADHESIVE PROPERTIES OF MALEIC ANHYDRID MODIFIED LNR (aluminium/aluminium)

Sample	% modified monomers units	Shear strength * (daN/cm²)
LNR AM 49	1.7	0.6
LNR AM 41	2.8	6.2
LNR AM 44	9.1	11.4
LNR AM 55	12.0	17.8
LNR AM 46	12.8	18.9
LNR AM 60	18.6	51.3
LNR AM 68	20.1	114
LNR AM 71	20.1	110
LNR AM 69	25.0	73
LNR AM 70	32.7	31
Referee sample **	-	194

LNR from centrifuged latex $\overline{M}v$ = 11,400

* mean value of 3 tests

** epoxy resin adhesive ("Araldite")

6.3. CONVERSION OF LNR TO A HIGH MOLECULAR WEIGHT ANTIOXIDANT

The conditions necessary to react 4-nitroso diphenylamine, NDPA, with natural rubber to give a rubber-bound p-phenylene diamine, and thereby an antioxidant resistant to water or solvent extraction, are well established. Despite some experimental difficulties associated with the high viscosity of LNR, these conditions were successfully applied to a 10 : 1 LNR/NDPA mixture to give a reaction product apparently free from unchanged NDPA. No attempt was made to isolate the adduct from the reaction product which was added into a tyre tread mix so as to give a level of 2 pphr antioxidant. This was compared with the same mix containing 2 pphr Santoflex 13, a conventional p-phenylene diamine claimed to be relatively resistant to extraction. Comparative test data for the two mixes are given in table 6.III.

TABLE 6.III

Comparison of Santoflex 13 and LNR/NDPA in tyre tread mix

	Antidegradent 2pphr	Santoflex 13	LNR/NDPA
	ML(1+4) 100°C	45	48
	Mooney scorch 120°C	18.5	10.5
	t_{95} 160°C	7.8	6.4
	Vulcanizate		
T.S. MPa	Initial	24.3	24.1
	Extracted in water *	25.2	24.8
	Extracted in toluene	23.1	24.8
	Aged 3d/100°C	12.6	9.6
	Ext.Water + Ageing	14.7	10.7
	Ext.toluene - Ageing	6.6	10.9
M100 MPa	Initial	2.22	2.70
	Extracted in water	2.45	2.78
	Extracted in Toluene	2.31	2.86
	Aged 3d/100°C	4.85	5.36
	Ext.Water + Ageing	4.92	5.42
	Ext.Toluene + Ageing	4.22	6..
DIN abrasion index	Initial	76	72
	Extracted in water	79	73
	Extracted in toluene	77	72
Fatigue life kc	Initial	207	149
	Extracted in water	272	106
	Extracted in toluene	49	106

* 7 days at ambient temperature

Consistent with previous experience with NDPA adducts, the mix containing the LNR product was more scorchy and faster curing than the Santoflex 13 mix. Initial vulcanizate properties were broadly similar though the LNR material gave a rather higher state of cure. Both abrasion resistance and fatigue resistance are known to be responsive to the presence of phenylene diamines ; for the former the LNR adduct is comparable with Santoflex 13 but fatigue performance is less satisfactory. Differences between LNR/NDPA and Santoflex 13 are also evident in protection against oxidative ageing ; LNR/NDPA gives lower tensile strength but higher modulus after ageing. However, the persistence of protection after solvent extraction is potentially the most important attribute of the LNR-based material. The data of table 6.III do provide some evidence for this in the better retention of tensile strength and enhanced modulus on ageing toluene-extracted vulcanizates and the much better retention of fatigue resistance after either water or toluene extraction. Rather surprisingly, DIN abrasion resistance is very little affected by extraction for either Santoflex 13 or LNR/NDPA.

An LNR/4 nitroso-diphenylamine adduct does show some promise as an antioxidant capable of becoming "network bound". In assessing the findings however, due account must be paid to two other considerations. First, experience both at MRPRA and elsewhere, has shown that in this area prediction of service performance from laboratory data is very uncertain. Second, and probably more important, the likely carcinogenic character of NDPA renders its commercial use, even as a precursor, subject to considerable constraints. Alternative chemical routes could doubtless be devised but these are most unlikely to be economically viable.

CHAPTER - 7

INDUSTRIAL APPLICATIONS AND DEVELOPMENTS

7.1. TECHNOLOGICAL WORKS WITH A VIEW TO INDUSTRIAL APPLICATIONS

The pilot unit existing in France has allowed sufficient amounts of LNR to be obtained. Technological studies therefore have been performed in the laboratory to detect potential applications in certain sectors.

7.1.1. Study on reinforcement - Processing

One of the limitations to the development of liquid rubber, of any origin, is the difficulty that exists in obtaining high mechanical properties. This is due to the problem posed by reinforcement where polymer-filler interactions are preponderant.

These interactions result from the shearing effects developped during the mixing of high molecular weight elastomers ; this is not observed with low viscosity products such as LNR.

Studies on formulation have shown that vulcanization by conventional systems does not lead to sufficient results ; it is necessary to use higher doses of sulphur and accelerators. It therefore is imperative to create crosslinks as short as possible ; so-called effective or semi-effective systems based on sulphur "donors" have thus been directed towards.

Two carbon black filled formulae have been particularly studied : the first with an accelerator system (Sulfasan R - DTMT - Accelerator CBS*) vulcanizing at 140° C, the second with Butyleight(**) vulcanizing at 100° C.

The second system should rather be selected for various reasons :

- it is liquid and easier to mix,
- vulcanization is possible at moderate temperatures, even below 100° C, avoiding thus an excessively fluidified mix that makes ingredients bubble or decant.

The mechanical properties are however lower than those of high molecular weight natural rubber. They are equivalent to those of a diisocyanate reticulated hydroxytelechelic liquid polybutadiene (table 7.I

(*) Sulfasan R : 4.4' dithiodimorpholine - DTMT : tetramethylthiurame disusphide-Accelerator CBS : N.cyclohexyl-2-benzothiazyl sulphenamide

(**) Butyleight : activated dithiocarbamates.

Table 7.I.

Comparative properties of natural liquid rubber
versus natural smoked sheet and synthetic liquid polybutadiene

	Liquid rubber Molecular weight		Smoked sheet	PB ARCO R 45 M
	$\bar{M}_w$: 9.300	$\bar{M}_w$: 20.000		
PROCESSING CHARACTERISTICS				
Blades	Sigma Blades		Z Blades	
Rotation speed (RPM)	64	64	64	
Filling level (%)	80	80	85	
TORQUE (m.g)				
Rubber alone	Near zero		3.200	
With processing aid	-		500	
After black addition :				
. maximal torque	700	900	3.500	
. stabilised torque	300	350	2.600	
CURING	(1)	(1)	(2)	(3)
Temperature (°C)	100	100	143	100
Time (mn)	15	10	15	90
MECHANICAL PROPERTIES				
Tensile Strength (daN/cm2)	125	153	286	105
Modulus 300 % (daN/cm2)	80	124	98	50
Elongation (%)	390	400	580	600
Tear resistance (daN/cm)	60	75	111	-
Shore hardness	70	73	62	57

CURING SYSTEM :

(1) . Butyleight - Sulfur
(2) : C B S - Sulfur
(3) : TDI (Tolylene diisocyanate)

Mixing conditions have been examined in a laboratory internal mixer. The following emerges :

- while mastication effects are detrimental to rubber-filler interactions, they are beneficial to energy consumption and rise in mix temperature ;

- it is necessary to use a non-pelletized carbon black ;

- it is preferable to use oil-impasted ingredients (zinc oxide and sulphur) for a proper dispersion to be obtained ;

- beyond 50 parts of carbon black, no substantial improvement in mechanical properties is observed.

Other fillers have been tested (silica, asbestos, mica). The mechanical properties obtained are poor, even in the presence of tensile agents (low breaking and tear strengths).

7.1.2. Obtaining low hardness vulcanizates at moderate temperature

By adapted formulations, low hardness vulcanizates (15 to 30° shore) can be obtained by vulcanization, at moderate temperature :

- a few hours at 100° C,
- 24 hours at 40-50° C,
- several days at ambient temperature.

These characteristics can be used to make certain mastics or pourable protection coating products.

Other accelerators of the same type as Butyleight (activated dithiocarbamates) can also be used and give similar mechanical properties.

7.1.2.1. LNR based compounds - low hardness

Vulcanized goods based on LNR were obtained having hardness varying from 15 to 30 shore A either at moderate temperature either at 100° C.

Table 7.II. gives formulations of compounds and hardness :

Table 7.II.

Formulations for low hardness vulcanizates

Compounds	1	2	3	4	5	6	7	8
Liquid rubber	100	100	100	100	100	100	100	100
Stearic acid	1	1	1	1	1	-	-	-
Zinc oxide	5	5	5	5	5	-	-	-
Butyleight	5	5	5	5	5	-	-	-
Sulfur	3	5	5	3	5	5	3	5
Merac *	-	-	-	-	-	5	3	5
Clay	-	-	-	-	-	10	-	-
Curing temperature (°C)	40	30	40	50	40	100	100	100
Curing time (h)	22	22	22	16	16	1	1	0,5
Shore hardness	30	20	35	25	25	35	20	15

* Merac : activated dithiocarbamate (liquid)

7.1.2.2. LNR based pourable compounds, confection of supple molds

Two compositions given on table 7.III were experimented, both lead to flexible moulds of fine look, into which good reproduction of the initial effigy can be obtained.

Table 7.III.

	1			2		
		Part	Part by weight		Part	Part by weight
LNR ($\bar{M}v$: 13,500)...	100	A	(100)	100	A	(100)
Paraquinone Dioxime.	3.75			3.75		
Plasticizer (SOMIL B)	150			150		
Chalk...............	500			-		
TiO$_2$...............	-			150		
PbO$_2$...............	20	B	(8)	20	B	(17)
Chalk...............	20			20		
Plasticizer (Dioctyl Phtalate)...........	20			20		

Part A of each compound was prepared in our laboratory internal mixer, and part B manually. Then A and B were blended by hand, just before pouring and before the vulcanization, which was carried out in a ventilated oven at 66° C during one hour.

The free mould surface in air contact remains sticky. This drawback can be overcome by covering the surface with either a silicon paper or a thin water layer.

7.1.3. Coating of ingredients for the rubber industry

Handling pulverulent ingredients destined to the rubber industry often causes emissions of dust impairing industrial hygiene.

The use of LNR as coating agent has been considered and a study has been carried out with two accelerators and two antioxidants ranked as "noxious". These coatings, achieved with a laboratory internal mixer and granulated with a blade grinder, for which the component/LNR ratio ranged from 75/25 to 90/10, have been used in compounds based on natural rubber, SBR and NBR. These coatings are properly homogeneous and more compatible with mixes than powders.

Besides, LNR can participate in reticulation, thanks to its chemical reactivity, avoiding thus a substantial modification in the mechanical properties of vulcanizates, which is likely to occur with certain coating binders such as oils or paraffin waxes. There are no losses due to dust emission which is of a definite economic interest.

LNR as a coating material for powdered chemicals

For these tests a sample of powdered CBS freshly obtained from the supplier was coated with 10 % LNR at IRAP and then returned to MRPRA for comparative tests. The coated CBS was undoubtedly less dusting than the standard material during both weighing and mill mixing. Tests for relative efficiency and dispersability were conducted in a mill mixed transparent gum formulation, (table 7.IV.), and a relatively soft HAF-filled mix prepared in a K2A Intermix at a batch weight of 28 kg (Table 7.V.). In both cases the coated material was considered to be 90 % CBS.

Table 7.IV.

Comparison of standard and LNR-coated CBS in transparent mix

SMRCV 50		100	
Active zinc oxide		0.6	
Stearic acid		0.6	
Sulphur		2.0	
Standard CBS	0.7		
CBS/LNR	-		0.78
ML(1+4) 100°C	20		20
Mooney scorch 120°C	35.4		35.0
Rheom. 160°C) $M_{HR}-M_L$	24.4		24.5
) t_{S1}	3.3		3.5
) t_{95}	5.0		5.4
Cure 6min/160°C			
M100 MPa	0.36		0.35
M300 MPa	0.83		0.82
M500 MPa	1.88		1.78
TS MPa	17.2		16.8
EB %	880		890
Hardness IRHD	33		32
Dunlop resilience %	82.6		80.5

Table 7.V.

Comparison of standard CBS and LNR-coated CBS in 28 kg black mix

Masterbatch in K2A Intermix	
SMR 20	100
HAF black	30
Dutrex 729	5
zinc oxide	5
stearic acid	2
Santoflex 13	2
sulphur	2.5

added in 2nd pass		0.5 standard CBS		0.56 CBS/LNR	
	No.	mean	st.dev.	mean	st.dev.
Rheom 160°C)$M_{HR}-M_L$	10	40.3	1.9	39.3	0.6
)t_{S1}	10	2.12	0.06	2.09	0.03
)t_{95}	10	7.79	0.19	8.39	0.17
Cure t_{100} 160°C					
M100 MPa	5	1.51	0.05	1.38	0.06
M300 MPa	5	7.59	0.37	7.21	0.22
TS MPa	5	27.9	0.6	27.0	1.4
EB %	5	607	7	601	17
Dunlop resilience %	5	80.9	0.5	80.3	0.5

In the gum mix, since the standard CBS gave no visual evidence for maldispersion as indicated by the appearance of characteristic brown spots, any improvement through the use of LNR-coated CBS can only be minimal. In terms of efficiency, the coated accelerator gave marginally lower tensile stress strain properties and resilence but the differences are probably within experimental error.

For the black mix a 2-stage process was used. In the first stage, all the ingredients other than CBS were added in the course of a 6 minute cycle. After cooling, CBS or LNR/CBS was added in a second pass through the mixer and by adding the CBS only half a minute before discharge and allowing only the minimum time on the dump mill, it was hoped to maximize any maldispersion of the CBS. Since visual assessment of the level of dispersion is clearly not possible in the presence of carbon black, replicate rheometer and vulcanizate tensile tests were used.

The results of these, expressed as mean and standard deviation are given in table 7.V.. Once again, as found with the gum mix, the state of cure in terms of rheometer torque or vulcanizate modulus developed by the LNR-coated CBS seems marginally less than for the standard form but, more important, only for the rheometer torque data is there any evidence for improved within batch homogeneity when LNR/CBS is used. Despite the very adverse mixing conditions used therefore any enhanced dispersability achieved by coating CBS with LNR must be very small.

7.1.4. Using LNR as a reactive plasticizer

LNR has been used as a substitute for the operating oil in mixes of high molecular weight elastomers.

7.1.4.1. Incorporation in NBR based compounds

20 % of depolymerized rubber was put in a NBR based compound containing 50 parts of carbon black. The results are compared to those obtained with an active plasticizer which is a nitrile liquid rubber commonly used with NBR.

Incorporating polyisoprene in concerned formulation boost lightly compound vulcanization.

It is established that swell values are similar for both compounds but extraction rate is lower for vulcanizates containing polyisoprene, it points out a better fit into rubber network structure (see table 7.VI.).

Mechanical properties are little affected incorporating depolymerized rubber and process features (compounding) are similar to those of synthetic active plasticizer. Mooney viscosities are the same (33 and 32).

Table 7.VI.

Volume swell (%) of NBR vulcanizate in various solvents

Plasticizer	Liquid natural rubber M_w : 9.100		Liquid butadiene nitrile rubber	
	Swelling (%)	Extraction (%)	Swelling (%)	Extraction (%)
Solvents :				
Ethyl acetate...	224	4	217	10
Toluol..........	288	4	227	9,5
Hexane..........	19	0	7	0,2
Chloroform.......	500	5	592	10

FORMULATION : NBR (BT 205) : 100 - Stearic Acid : 1
Zinc oxide : 5 - Carbon black (SRF) : 50
MBTS : 1,5 - Sulfur : 2 - Plasticizer : 20

7.1.4.2. Incorporation in SBR based compounds

In a SBR based formulation containing 20 parts of Dutrex V$_2$ (mineral processing oil), oil was replaced by same quantity of depolymerized rubber having a molecular weight of 9,300. Table 7.VII. points out main properties of these compounds after vulcanization at T 90 and 30 min. at 145° C.

Compounds containing low molecular weight rubber vulcanizes more rapidly than standard SBR formulation and mechanical properties are similar. Swelling values in toluene are lightly higher than with compounds containing Dutrex, but again extraction rate is kept lower.

Table 7.VII.

Mechanical properties and volume swell (%)
of SBR vulcanizate plasticized with
liquid natural rubber and mineral oil (Dutrex V2)

Plasticizer	Liquid natural rubber		Dutrex V2	
ML 1+4 (100°)	38		44	
Curing time at 145°C (mn)	T 90 : 13,5	30	T 90 : 21	30
Properties				
Tensile strength (daN/cm²)	232	225	198	199
Modulus at 300 % (daN/cm²)	40	46	38	44
Elongation (%)...........	800	730	730	700
Tear resistance (daN/cm).	37	37	35	35
Shore hardness...........	53-49	53-49	51-45	51-47
Swelling (vol.%) in toluol	351	365	289	302
Extraction (%) in toluol	8	8	15,7	15,8

FORMULATION : SBR (S 1501) : 100 ; Stearic acid : 2
Zinc oxide : 3 ; Antioxidant BLE : 0,35
Antioxidant AKROFLEX CD : 1 ; Sulfur : 1,75
Accelerator CBS : 1,2 ; Accelerator DTMT : 0,12

7.1.4.3. LNR as a vulcanizable plasticizer in natural rubber

Comparative data for LNR and a typical hydrocarbon plasticizer at both low and moderate levels in a tyre tread mix are given in tables 7.VIII. and 7.IX.

Table 7.VIII.

Comparison of LNR and oil in a tyre tread mix
Compound formulation and mixing behaviour

	1	2	3	4
SMR 20	100	100	85	85
Dutrex 729 oil	5	-	20	-
LNR	-	5	-	20
N220 black	45			
zinc oxide	5			
stearic acid	3			
Santoflex 13	2	--------	--------	------>
CBS	0.5			
S	2.5			
Dump temp °C	150	151	129	134
Peak power kW	12.7	12.5	10.3	9.1
Specific mixing energy kWh/l	0.564	0.569	0.486	0.488
Cabot black dispersion	B1-2	C1-4	D/E1-3	C1-4

Table 7.IX.

Comparison of LNR and oil in tyre tread mix
Vulcanizate properties

	1	2	3	4
Hardness IRHD	65	65	62	59
M100 MPa	2.50	2.44	2.13	2.13
M300 MPa	12.4	11.9	9.88	9.03
TS MPa	28.4	27.2	24.4	23.1
EB %	560	556	583	578
Dunlop resilience %	63.5	65.1	59.3	58.9
Ring fatigue kc	139	128	147	193
DIN abrasion index	96	93	74	73
Comp.set 1d/70°C %	33	33	38	37
± 1%) G* MPa	3.3	4.9	5.0	5.2
20Hz) δ	9.6	9.2	14.3	12.5
Aged 3d/100°C) M100 MPa	4.03	3.97	3.60	3.92
Aged 3d/100°C) M200 MPa	9.46	9.70	8.23	8.74
Aged 3d/100°C) TS MPa	12.7	13.4	8.8	11.0
Aged 3d/100°C) EB %	253	252	208	239
% Toluene extract *	10.3	11.1	23.3	19.6

* [illegible] days at [illegible] 100° C

In broad terms, the two materials produce mixes or vulcanizates having very similar properties, but two significant differences can be discerned. First, there are rheological differences ; while compounds containing LNR or oil have similar Mooney viscosities, at higher shear rate LNR gives a higher viscosity and greater nerve or elasticity and, consistent with this, a higher green strength or elongational viscosity (table 7.X.).

Table 7.X.

Comparison of LNR and oil in a tyre tread mix
Uncured properties

	1	2	3	4
ML(1+4) 100°C	71.5	72.5	52.5	55
ML(1+4) 120°C	65	64.5	48.5	50
Capillary rheometer shear rate 900 s^{-1}				
L/D=2)Viscosity MPas×10^3	4.21	4.52	2.48	3.24
L/D=2)Die swell %	223	223	191	230
L/D=20)Viscosity MPas×10^3	1.08	1.12	0.58	0.87
L/D=20)Die swell %	68	63	74	73
Green strength				
M100 MPa	0.55	0.57	0.38	0.43
M300 MPa	1.19	1.46	0.72	0.96
M500 MPa	2.95	3.33	1.71	2.32
Cure behaviour				
Mooney scorch 120°C min	24.7	23.2	24.9	18.7
Rheom. 160°C) $M_{HR} - M_L$	28.6	26.5	23.8	23.4
Rheom. 160°C) t_{S1}	2.6	2.4	2.4	2.2
Rheom. 160°C) t_{90}	8.1	8.0	8.1	7.3
Rheom. 160°C) t_{95}	9.3	9.2	9.2	8.3

This feature could well be advantageous in handling and conferring resistance to distorsion on relatively soft mixes. The vulcanizate property data of table 7.IX. reveals very little difference between materials containing LNR and Dutrex 729. The sole exception to this is in resistance to oxidative ageing, where LNR shows an improved performance. The reason for this is not obvious but possibly an increased proportion of LNR becomes bound to the network during ageing (vide infra).

As shown in table 7.XI., these two advantages are also evident when LNR is compared with other typical hydrocarbon plasticizers. Two other benefits, neither easily quantified but likely to accrue to LNR if used as a plasticizer, can be envisaged. Though rather dark in colour, LNR will not produce the discolouration and migratory staining associated with the use of highly aromatic oils and is likely to be less volatile in extended service at relatively high ambient temperature than the light coloured non-staining paraffinic oils preferred when colour and staining are important.

Table 7.XI.

Comparison of LNR and hydrocarbon oils in a tyre tread mix

*					
SMR 20	100	80	80	80	80
LNR	-	20			
Dutrex 729	-		20		
Sunthene 4240	-			20	
Petrofina 2059	-				20
ML(1+4) 100°C	67	51	49	69.5	47.5
Green strength					
M50 MPa	0.44	0.38	0.28	0.30	0.28
M100 MPa	0.43	0.40	0.30	0.34	0.30
M200 MPa	0.49	0.46	0.34	0.40	0.38
M300 MPa	0.73	0.64	0.45	0.52	0.54
M400 MPa	1.22	0.95	0.69	0.75	0.83
Vulcanizate properties					
) M200 MPa	5.68	5.24	4.57	4.89	5.10
Unaged) TS MPa	28.6	24.8	23.1	23.3	22.8
) EB %	560	590	585	580	560
) M200 MPa	9.1	10.4	7.6	8.3	-
Aged) TS MPa	15.3	15.6	9.6	10.4	-
3d/100°C) EB %	270	305	245	240	180
) M200 MPa	10.5	10.5	8.6	8.8	11.2
Aged) TS MPa	19.3	17.5	14.4	14.3	14.2
7d/90°C) EB %	320	305	315	295	255
) M200 MPa					
Aged) TS MPa					
28d/70°C) EB %					

* Other ingredients as Table 7.VIII.

The most obvious interpretation of the general parity in vulcanizate properties between vulcanizates containing LNR and oil is, that because of the relatively low molecular weight of LNR as compared to normal NR, LNR like a normal plasticizer, is not in fact vulcanized into the crosslinked network. This contention is apparently confirmed by the equivalence between oil and LNR in the toluene extraction data of table 7.IX. However, these data were obtained under relatively severe extraction conditions which were subsequently shown to give rise to concurrent network degradation. Indeed, it has proved impossible to obtain unequivocal data indicative of the proportion of LNR bound into the network during vulcanization. It seems possible that in black-filled mixes some at least of the LNR becomes closely associated with the filler and therefore relatively difficult to extract.

As shown in table 7.XII., under relatively mild extraction conditions, a much smaller proportion of LNR is extracted from either gum or black-filled vulcanizates.

Table 7.XII.

Dependence of extract ability of LNR on crosslink density

	7	8	9	10	11	12	13	14
SMR 20	100	100	100	100	80	80	80	80
LNR	-	-	-	-	20	20	20	20
S	2.5	3.75	5.0	6.25	2.5	3.75	5.0	6.25
CBS	0.5	0.75	1.0	1.25	0.5	0.75	1.0	1.25
+								
Gum mix								
M200 MPa	0.97	1.44	1.97	2.55	0.52	0.81	1.06	1.42
% extractable*	2.8	2.3	2.0	2.1	6.3	4.4	3.8	3.2
Tread mix								
M200 MPa	6.05	8.62	9.62	12.1	5.00	7.84	9.78	11.4
% extractable*	2.1	1.6	1.5	1.5	4.7	3.5	2.9	2.7

* 7 days in toluene 23°C

\+ ISAF 0 or 45; Zno 5; Stearic acid 2

As would be expected, the proportion decreases as the level of crosslinking is increased but as a corollary this implies that covulcanization of the LNR is incomplete at the lowest (normal) curative level, CBS = 0.5 ; S = 2.5. Enhanced covulcanization of LNR would also be anticipated as the ratio LNR/NR is raised and this is evident in the data of table 7.XIII. State of cure, as indicated by rheometer torque increase, $M_{HR}-M_L$ decreases as the proportion of plasticizer is increased but this feature is far more apparent with the non-reactive oil. Rather surprisingly rate of cure, t_{95}, which is rather higher for mixes containing low levels of LNR (cf. table 7.X.) does not continue to increase with higher levels.

Table 7.XIII.

Comparison of higher loadings of LNR or oil in a tyre tread mix

*								
SMR 20	80	75	70	65	80	75	70	65
LNR	20	25	30	35	-	-	-	-
Dutrex 729	-	-	-	-	20	25	30	35
Final mix								
Cabot dispersion	A1	A1	A1	A1	A1-2	B1-3	B1-3	B1-3
ML(1+4) 100°C	46.5	39.5	36.5	34	41	38	32.5	29
Rheom. 160°C } $M_{HR}-M_L$	26.0	25.7	24.5	23.5	24.8	22.5	20.9	19.9
} t_{S1}	1.8	1.9	1.8	1.8	2.1	2.2	2.3	2.3
) t_{95}	7.2	7.3	7.3	7.1	8.3	8.3	8.3	6.5

* other ingredients as table 7.VIII.

Relatively high levels of plasticizer can also be used in compounding for the hard vulcanizates used for some engineering applications. Comparative data for LNR, hydrocarbon and ester plasticizers and factice are given in table 7.XIV.

Table 7.XIV.

Comparison of LNR and other plasticizers in a 80 IRHD mix
Compound formulation, mixing & uncured properties

SMRCV 50	100	70	70	70	70
LNR	-	30	-	-	-
Dioctyl adipate	-	-	30	-	-
Dutrex 729	-	-	-	30	-
Factice	-	-	-	-	30
Naphthenic oil	6				
FEF black	80				
Zinc oxide	5				
Stearic acid	2				
Santoflex 13	3				
Wax	2	------	-------	-------	----`
CBS	0.8				
S	3.77				
PVI	0.3				
Banbury) dump temp °C	140	105	102	136	132
) peak power kW	13.9	11.0	7.9	6.9	12.4
masterbatch) specific energy kWh/l	0.48	0.42	0.45	0.50	0.43
Final mix					
ML(1+4) 100°C	67	45	49.5	32.5	80
Rheom 160°C) $M_{HR}-M_L$	44.8	42.5	46.0	41.6	43.1
) t_{S1}	2.5	2.5	2.3	2.5	2.0
) t_{95}	7.3	7.0	6.4	7.2	8.0
Green strength M300 MPa	3.86	3.06	2.51	2.00	3.77
L/D = 2) Viscosity MPas x 10^3	2.31	1.33	1.58	1.11	2.67
950 s^{-1}) Die swell %	46	31	29	26	17

The low toluene extract figure for LNR suggests that under these favourable conditions of high curative level and relatively high LNR/NR ratio, most of the LNR is incorporated in the network. The plasticizers are very diverse in nature and this diversity is reflected in the properties before and after vulcanization ; in the event the choice of plasticizer could well depend on the property or properties of the vulcanizate regarded as critical for the application in question. Under these circumstances the positive attributes of LNR are, high green strength, high tensile strength, excellent fatigue resistance and low extractability. As noted earlier an ester plasticizer will always be preferred if very low temperature performance is at a premium.

Conclusion :

While the actual level of covulcanization in an LNR/NR mix has proved difficult to determine and there are problems therefore in fully interpreting the data obtained, there is evidence for specific technical advantages of LNR over conventional plasticizers. In particular, green strength is higher and retention of tensile strength after ageing improved. Other less quantifiable benefits, such as reduced vulcanizate discolouration and lower loss of plasticizer by volatilization can be envisaged.

7.1.5. Various studies

LNR has also been used to prepare ebonites and cellular rubber for which implementation is made easier :

- in the case of ebonites, components are more easily mixed,
- in the case of cellular rubber, swelling level is improved.

7.2. COMMERCIAL DEVELOPMENT

7.2.1. Introduction

The contacts aimed at either confirming or creating, determining and identifying needs for modified or unmodified LNR in large industrial sectors a priori considered as being liable to use it. Their objective was also to induce the prospective manufacturers to perform tests on a gratuitous basis and lead thus to a request for samples provided by the small pilot unit existing in France and later by the IRCA pilot plant in Côte d'Ivoire for larger amounts. The latter has been started up within the period of time specified by the contract. But because the duration of the contract has been reduced from 3 to 2 years, it will not be possible to obtain in time all the results of the studies carried out by internal potential users, particularly for the supply of industrial-sized samples produced by the plant of the Côte d'Ivoire.

For a new product as well as for a product competing preexisting products on the market, manufacturers may take several months to one year to response, considering their motivation and the duration of laboratory tests. The manufacturer's motivation depends on factors such as technical improvement in the product proposed, immediate or non-immediate solution to a precise technical problem, price and availability. As this report is being written for instance, all the results of the tests conducted by manufacturers are not known.

Besides, in front of a considerable potential market, some manufacturers have rised two problems. The first relates to the size of the production unit that is not sufficient in their opinion. The second concerns the probability of building an actual industrial-sized plant capable of producing one to several tons of LNR per operation.
This uncertainty has sometimes influenced the decision to undertake tests.

The results described below reveal a few applications corresponding to potential markets to develop.

7.2.2. Results of the prospecting campaign

7.2.2.1. Definition of the sectors to prospect

At the beginning, because of the experience gained before the contract in LNR achievements, some preference sectors have been defined. They were the following :

- ingredient coating : for reasons of hygiene, safety, economic cost and productivity, many products are used not in pulverulent form but bound by an agent inert towards the end product. Using liquid rubber as coating binder participating in the operating process was to give advantages to promote ;

- the rubber industry was to be interested in liquid rubber as reactive plasticizer ;

- adhesive industry : liquid rubber could be used as plasticizer of hot-melt resins. In this industrial sector, the aim was to prepare needs for so-called "second generation products" made with liquid rubber ;

- paint and varnish industry : "second generation products" were to find interesting outlets in this sector too ;

- cable industry : for specific applications and determined packaging, liquid rubber could be used in the composition of cable filling products ;

- waterproofness : liquid rubber involved in the composition of special bitumeus would participate in the development of new waterproofness products.

The main firms involved in these sectors have been selected with the help of various national trade unions which provided lists of members. They have been gradually visited while the contract lasted.
A general technical data list on LNR was given to each firm visited.
In answer to the manufacturer's request, LNR cost has been announced as ranging from 25 to 35 F/kg (scale 200 kg/week).

After a few months however, it seemed necessary to focus on better-adapted sectors; to approach new sectors excluded at the beginning; and to give up those which were probably more interested in "second generation" products derived from LNR chemical modification.

This selection has been carried out in cooperation with Dr. Mullins, UNIDO Technical Advisor.

It has been established taking into account the observations received during the visits made to various firms willing to perform technical tests complementary to those of IRAP and according to the first results of the estimating tests.

It seemed that, in these sectors, quite a large number of firms were prepared to cooperate actively. The following sectors corresponding to possible LNR uses have been selected for deepening purposes :

1. Reactive plasticizer :

LNR used as a low concentration blending product can have two applications :

a. non-extractible reactive plasticizer,

b. reactive plasticizer for high hardness mixes.

These types of application concern many firms in the technical and car rubber processing industries.

2. Enduction :

LNR used in formulations makes it possible to adjust viscosities and limit solvent consumption by work at concentrations in formulated product of around 80 %.

3. Adhesives and mastics :

As far as adhesives are concerned, LNR has interesting qualities, especially thanks to its tackyfying capacity, high solubility and filler acceptance.

As far as mastics are concerned, LNR is interesting because it can be cold vulcanized (bi-component systems).

4. Binding agents for abrasives :

In order to make rubber-based abrasive grindstones, a collaboration between manufacturers and IRAP has developed in technical tests.

5. Supple foams :

Using LNR in these applications makes it possible to approach the expansed foam and shoe industry (utilization in some sub-layers).

6. Binding agent for coating purposes :

Coating an ingredient with LNR can facilitate its dispersion in mixes.

The main sectors abandoned therefore have been the following : cables, paints and waterproofness. They mainly were sectors of application for maleic anhydrid or chlorine modified LNR.

It also seemed necessary to estimate two fields in which manufacturers had not been contacted yet :

a. flexible moulds, for which LNR was supposed to be capable of competing with silicones on both the technical and economic standpoints in some applications,

b. ebonites, which are relatively easy to make with LNR.

Besides, as the visits took place, observations on the difficult processing of LNR by conventional equipment suited to dry rubber were made. That is why it was decided to contact equipment manufacturers in order to define LNR pumping possibilities. Thanks to a large specialized firm, it has been possible to check the pumping capacity of untreated LNR and that of the master batch without pre-heating. This type of information was transmitted to the manufacturers ; it eliminated some hesitations and sometimes helped to obtain free estimating tests.

7.2.2.2. Assessment of the contacts with manufacturers

A total of at least 90 firms have been contacted and 75 of them have wished to receive a sample of LNR in variable amount. However, paint firms, more interested in chlorinated LNR, and equipment manufacturers have not been supplied with the product.

Out of the 75 above-mentioned firms, some wished a sample out of mere politeness and curiosity. Others, which really wanted to undertake an estimate could not do it for various reasons (economic problems, lack of time, restructuring, moving...). In other words, the number of firms having actually performed tests is 50, that is 67 % of the firms sampled. As part of their test campaign, 12 of them (i.e. 24 % of the firms having conducted tests) have wished IRAP to cooperate as to increase their knowledge of the product.

Table 7.XV. shows, by sector of activity, the distribution of the firms contacted as compared to the various possible uses considered for LNR.

7.2.2.3. General comment on the manufacturers' attitude towards the product

Before we describe the results obtained in details, it seems indispensable to report the observations made by almost all the manufacturers contacted and to ask a few basic questions which appeared more and more clearly as the prospecting campaign was going on.

They concern :

- first, the UNIDO project ; second, the LNR itself, and third, the prospecting area.

Table n° 7.XV

Contacted companies distribution

Industrial area	Number of contacted companies	Number of sampled companies	Possible use for the LNR
Rubber chemicals industry	3	3	Binding agent
Waterproofness applications industry	2	2	Formulation's ingredient
Wire industry	2	2	Ingredient of filling product for cable
Adhesives and glues industry	7	7	Formulation's ingredient
Tapes industry	7	7	Formulation's ingredient
Caulks industry	3	3	Formulation's ingredient
Molding industry	6	4	Formulation's ingredient for supple moulds
Grinding wheels industry	3	2	Abrasive particles binder
Soles and shoes industry	3	3	Soling's ingredient
Rubber automotive industry	9	8	Processing aid reactive plasticizer
Rubber technical industry	27	24	Processing aid reactive plasticizer
Spreading, flocking industry	6	6	Ingredient of coated fabrics compounds
Supple foams industry	2	1	Formulation's ingredient
Lining's industry for cylinders and tanks	3	2	Processing aid for hard coatings and ebonite
Leather industry	1	-	-
Paints and varnishes industry	2	-	-
Manufacturers of equipments	4	1	-
Total	90	75	

a. The project and its consequences :

- As regards the manufacturers' general attitude towards UNIDO project, we have noted a definite interest in the idea of searching for a new form of natural rubber.

- Among the greatly interested manufacturers, some would have liked to make sure that the process and production had exclusive rights so as to be protected from competition in their own sector of activity.

- At the same time, the production capacity of the pilot plant involved seemed reasonable for most manufacturers ; but for others, if manufacturing was to be immediately launched, this capacity would be too low as compared to the requirements they detected ; they wished to be given an assurance that this capacity would be rapidly increased to satisfy their markets for fear of being surpassed by their competitors (sector of the glues and adhesive ribbons for instance).

- Ultimately, the price decided upon in collaboration with IRCA and UNIDO of 25 to 35 F/kg, although we always insisted on the fact that it was a "pilot" price likely to decrease if production was larger, has been often considered as being too high. This price prevented LNR from being used as a substitute for the products currently used and much cheaper, in spite of higher qualities often admitted. As far as conventional rubber processing is concerned, LNR, as plasticizer, coating agent or basic vulcanizate element, has been marginally used in small tonnages. On the other hand, in the paint and adhesive industries and, more generally speaking, in the manufacturing of elements with a high value added, the price did not seem to be an insurmountable obstacle if the LNR-based product had indisputable technical qualities.

b. LNR itself :

We have also noted the general attitude of the manufacturers contacted towards the product itself. For applications such as adhesives, flexible moulds, binding or coating agents and special mastics, the aspect of LNR was an incontestable technical advantage. On the contrary, in the case of the manufacturers of the rubber industry, its aspect was very disconcerting for technicians used to handle solids, even pulverulent, or liquids, most often pumpable. A systematic objection has been made as to the absence in workshops and laboratories of machines suited to such a product, especially at the mixing stage. In these times of world economic crisis, no firm wishes to put large investments in equipment if a short-term profitability is not certain. A presentation of the product, making it easier to handle should possibly be examined.

c. The prospecting area :

As an end to these observations of a general matter, we should mention that, after frequently meeting manufacturers whose firm was a subsidiary of large international groups, they often suggested we should contact their parent company abroad. The decision UNIDO took to limit the contract to two years instead of three, did not allowed us to organize a large scale prospecting campaign on an international level.

7.2.3.1. Adhesives

7.2.3.1.1. Adhesive ribbons :

LNR has aroused a very large interest in this sector. Its advantages are the following :

- appreciable easy handling due to its liquid consistency. It is a pumpable product ;

- suppression of the usual work of natural rubber peptisation thanks to gum "milling" ;

- possibility of working on formulations with a very high dry extract content (up to 85 %), never reached yet with the elastomers known ;

- possibility of chemically modifying the product by grafting or chlorination.

However, there are disadvantages too :

. owing to its colour, the products prepared can only be dyed ;

. the conventional formulations for natural rubber cannot be used ;

. as a main elastomer, cohesion and tack supply are far from being sufficient.

Attempted blendings with high molecular weight rubber should compensate for the lacking cohesion observed. A research programme of applications in this field will have to be undertaken with the manufacturers concerned. LNR is also interesting as reticulated product. This type of manufacturing requires an ultra-rapid reticulation system which is difficult to define. The use of reticulating agents is indispensable but complicated. Electronic bombardment can be resorted to but is expensive in view of the heavy investment it supposes. It should be noted that the manufacturers have admitted they were "favourably surprised" by the product. Also, three adhesive ribbon manufactures, including two multinationals are still interested in LNR at the end of 1985 and wish the tests be continued, despite its deficiencies of cohesion and tack.

7.2.3.1.2. Mastics :

Large samples of LNR have been supplied to a Dutch firm for the manufacture of mastics. LNR has good wetting properties and its use in formulation of low cost/performance mastics and sealants may provide a substantial though possibly deducing market for LNR provide its prices is competitive with the other elastomers used at the present time and its supply can be guaranted.

7.2.3.1.3. Glues :

Generally speaking, the opinion is unfavourable. LNR is usually considered as a poor plasticizer as compared to other cheaper and less fragile products. Its heat and ageing resistances are unsatisfactory.

In hot melts, its colour is disadvantageous and it is little compatible. In solvent-adhesives and emulsion-adhesives, considering that it cannot lead to the total replacement of usual tackyfying resins, it has no economic interest, especially since it gives to formulations a deficiency of cohesion and tack. It therefore is qualified by manufacturers as an "expensive product with common properties" or as an "inert product". The main reproach is its totally insufficient sticking supply.

7.2.3.2. Cable manufacturing

The use of LNR had been considered as a filling material. The idea was quickly abandoned following the results of the test conducted by the largest French cable manufacturing plant. It observed a difficult incorporation without pre-heating, a decreased ability of formulations to withstand a high filler rate, and a marked embrittlement to ageing. This sector therefore was excluded because natural rubber only amounts to 10 % of its consumption.

7.2.3.3. Coating of ingredients for the rubber industry

Owing to the arguments expounded before, LNR was rather favourably received in this sector. It should however be mentioned that this attitude came from the possible users of coated products rather than from coating manufacturers. The latter had a few reservations because of their inadequate equipment, the LNR price announced and the difficulties of implementation requiring a dilution with paraffin oils. In short, it is a relatively interesting product on which two firms still wish to work today ; their main aim was to achieve a process of continuous coating which would be a total innovation in this sector.

7.2.3.4. Supple foams

In this case, the results are satisfactory when the manufacturers make an effort to readjust their usual formulae according to the quality of the LNR added. The products obtained have an excellent remanent deformation to compression. LNR can be regarded as a viscosity stabilizer. When the basic formula is not modified, the compounds obtained are so sticky that they do not swell despite the supply of swelling agents. Owing to the fierce competition prevailing on this market, the manufacturers involved required the information supplied be confidential ; the technical advantage obtained must be indisputable to justify the relatively high price of LNR.

7.2.3.5. Abrasives

The use of LNR as binder of abrasive grains had been examined from the outset of the contract. In France, the market of rubber binder mills is declining to the advantage of mills made according to other techniques. However, they still keep a small share of the market which is supplied by imports. The development of a French production therefore is still of a medium interest on condition that it is possible to obtain technically a reduced manufacturing time to make production profitable.

In addition, several manufacturing criterious have to be taken into account such as behaviour in overspeed, mechanical resistance, parallelism, density, weight.... Standards have to be respected. At the end of 1985, development works are going on in collaboration with one manufacturer and contacts have been made in England and in the United States.

Formulated LNR to obtain ebonite, hard rubber, can provide a solid bond of abrasive grains, mill components.

Corundum or silicon carbide based mills have been made with variable LNR and vulcanizing agent contents to obtain a binding agent of the ebonite or semi-ebonite type.

Speed and milling tests have been carried out by a manufacturer of abrasive wheels who made a few observations :

- our manufacturing method does not provide a sufficient accuracy in dimensional control,
- relatively quick wearing out,
- excessively strong smell of burnt rubber.

Consequently, additional tests are necessary.

7.2.3.6. Enduction

It is the sector where collaboration with manufacturers was established the quickest. As in the case of adhesive ribbons, the aspect of LNR made it very attractive since it should make it possible to substantially reduce the amount of solvent to add. However, several difficulties had to be solved : implementation conditions had to be defined again owing to the failure of the equipment to adapt to an easy filler incorporation, and despite everything, use of solvents in limited amount.

Besides, the main difficulty to solve was the development of a vulcanization system suited to LNR to remove or reduce the duration of the plastic phase while the temperature rises during vulcanization ; the latter must be extremely rapid in order to allow enduction, at the tunnel exit, to be sufficiently reticulated and non-sticky so that the coated product can be rolled up without risk. Resistance to ageing is often lower than that of synthetic elastomers which are increasingly used in this field.

Through a close and continuous collaboration with one coating manufacturer, it has been possible to achieve thanks to LNR a thick enduction in a few layers by scraping. While satisfactory enductions are obtained, the flexibility and mechanical properties of the products obtained do not correspond at all to the present requirements of the French market. A possible use of LNR has consequently been suggested in very specific applications such as self-adhesive enductions. However, this can be possible only if the product reaches a competitive price.

7.2.3.7. Rubber processing industry

This sector involves the manufacturers of technical and pneumatic articles as well as the shoe industry. LNR can meet certain manufacturers' requirements as :

1. a non-extractable reactive plasticizer : for elastomers other than NR, SBR and NBR, its use is limited since it may, owing to its insaturation, perturb vulcanization ;

2. a processing aid for the manufacturing of high-hardness compounds since it can facilitate implementation and milling conditions ; the vulcanization system must be adjusted. It gives to uncured rubber a higher sticking capacity and to vulcanized rubber particular damping properties.

Two branches of this sector have given rise to studies in collaboration with manufacturers :

- the car industry : the use of liquid rubber has been studied to make high-hardness compounds, for which it is necessary to establish a fair compromise between the amount of carbon black, relatively high to obtain the mechanical properties required, and the amount of processing oil to provide a proper mould flowing.

The first tests on the use of LNR as a processing aid, conducted by the manufacturers concerned, have shown a few drawbacks (drop in mechanical properties, although hardness is unchanged, decrease in operating safety despite an interesting drop in compound viscosity favourable to a good implementation). A technological study on formulation has been undertaken in France. The drop in mechanical properties has been substantially decreased and a scorching time acceptable for the compound has been restored.

- the shoe industry : like some components used in the car industry, shoe soling requires the use of high-hardness compounds.

In this sector, LNR has also been examined as a processing aid. Following the tests conducted by manufacturers, the same observations appeared regarding final mechanical properties, although implementation was markedly improved. In this case too, a formulation study made it possible to make up for most of the drop in mix performances. However, abrasion properties are lower.

7.2.3.8. Flexible moulds - Pourable compounds

Some industries use flexible moulds made in synthetic rubber, particularly silicone which price is relatively high for reproducing parts.

Formulations of the bi-component type capable of producing flexible moulds with low hardness materials have been developed.

Bi-component compounds made with LNR are today a cheaper variant of generally used silicones, with markedly different performances, reserved, at the present stage of development, for the manufacturing of moulds either prototypes or produced in very small quantities. The working life of flexible moulds is markedly lower since the formulated material does not tolerate properly the aggressive contact of polyurethan casting resins. It is indispensable to resort to a stripping agent. The design of formulations is still being examined today in order to make handling as simple and reliable as possible. With the help of a small artistic and industrial moulding manufacture, the problem could be roughed out improving setting times and reproduction fidelity. Bi-component pourable compounds, based on LNR, capable of vulcanizing at ambient temperature in a few hours or more quickly with slight heating (60° C) have been tested.

Elastic, flexible moulds are obtained which are easily recoverable even on tortured parts. Later, these moulds made it possible to obtain faithful reproductions of medals, glass in cut crystal, wood pieces showing detailed veins, by casting plaster or polyurethan resin.

A prototype stamping has been made comprising various defects (stria, cross pieces, frosted places) to estimate whether mould reproduction was faithful. Samples of pourable mix have been sent to the manufacturer involved.

7.2.4. Conclusion

We can define several sectors where LNR will be of an industrial interest. The latter took shape by a new request for samples of the product made by the pilot plant of the Côte d'Ivoire;the manufacturers wished to continue their estimate by life-size tests.

- Car industry :

A large French tyre manufacture asked for 200 kg of the LNR made in the Côte d'Ivoire . It seems to be interested in high molecular weight LNR and wished to make sure the supply from the Côte d'Ivoire was reliable. It is impossible to anticipate a possible consumption of natural rubber in this firm, especially since its exact use will never be revealed owing to the systematic secret this large firm surrounds itself with.

- Cellular rubber :

A manufacturer specialized in foams has become interested in LNR following an order for which, by using the conventional cellular technology, he was not competitive. Despite the technical problems of LNR weighing and handling, his first tests in the laboratory seemed interesting enough for him to ask for an additional sample. He received around 20 kg to perform life size complementary tests and requested the marketing service of his firm to examine the possibility of selling cellular rubber made with LNR. However, he has reservations about his consumption needs, being the latter dependent on the LNR price which will be proposed to him.
The present pilot price is an absolute obstacle.

- Structural adhesives and adhesive ribbons :

A large multinational firm, leader in the manufacturing of epoxy glues, is keenly interested in the role of softening agent LNR can play in its sector. For the time being, it meets technical problems for which it has requested the help of IRAP. But it has already asked for an additional sample to continue its estimate in other fields.

Another very large firm, favourably surprised by the possibilities of incorporating LNR in formulations of adhesive ribbons intends to continue its estimate.

In both cases, it is too soon to think of consumption figures ; however, it is certain that the adhesive market in general is changing and that competition is stiff ; if certainties of regular LNR supply are not given soon, these firms will turn towards other products.

- Pourable compounds :

A firm resaling ingredients for rubber processing, located in the East of France, has detected in its zone of influence some interest in pourable compounds by crystal makers. They frequently use moulds to reproduce ancient parts and cannot employ silicones. This firm is thinking of creating a subsidiary to sell ready-to-use pourable compounds in kit. It intends to provide the French and German markets. The project is still being studied today and it is too early to forecast consumption.

7.2.5. Economic aspects of Liquid Natural Rubber - Production and Markets

7.2.5.1. The present market for Liquid Natural Rubber

A number of firms are known to produce Depolymerized NR, "DPNR", for "in-house" use but only two have been identified that manufacture DPNR on a commercial basis. They are Hardman Inc. (Bellville, New Jersey, USA) and Chloride Lorival Ltd (Little Lever, Greater Manchester, UK). DPNR manufacture originally accounted for a major part of the activity of both firms, but is now only a small part. The primary area of activity for Hardman Inc. is now the development, manufacture and sale of epoxy resins, mainly for use in adhesive and coating formulations. The firm was founded in 1906 to manufacture tyres, hard rubber goods and hot water bottles and it was the firm's founder, K.V. Hardman, who developed the process for DPNR manufacture which lead to the first commercially available supplies of DPNR in 1923. This process is beleived to be based on the extensive mastication of natural rubber in oxygen. The manufacturing process used has never been revealed but one of Hardman's patents, for manufacturing goods from DPNR, refers to the use of temperatures of 290°C for 2-4 hours in the production of DPNR. This process was refined and developed into its commercial form which has changed little to the present day. Though the emphasis of the firm has shifted from DPNR manufacture to the marketing of epoxy resins, its philosophy has remained unchanged. This philosophy has been to keep the firm within the control of the family; the third generation are now the chief officers of the firm. This has meant keeping it a privately owned firm which has placed significant constraints on growth and expansion.

Chloride Lorival (originally Lorival Ebonite Ltd) first manufactured DPNR in 1953. During the 1920s and 30s at least two processes were developed in the UK for the manufacture of DPNR, both of which were taken as far as trial production runs. However, neither process was developed commercially. One of these processes, patented by Stevens and Stevens in 1933 to produce "Rubbone", was re-examined in the post-war period, but discarded in favour of a mechanical process based on the extensive mastication of natural rubber at elevated temperatures in the presence of oxygen.

A process similar to the one used at Hardman. The process used by Chloride Lorival was developed by Rubber Technical Developments, the development unit of the then British Rubber Producers' Research Association and British Rubber Development Board. Confusingly, the DPNR produced by this process was also called "Rubbone". In this process the rubber is initially masticated in a conventional 2-roll mill or internal mixer until its Mooney viscosity is 20. It is then worked in a Z-blade mixer at 120-140°C for 6-9 hours until its viscosity is in the range 50-70.000 poises. Finally the material is heated in a suitable reactor for 120-160 minutes at 250-300°C. This produces a material which has lost much of its rubbery characteristics but is pourable at room temperature and has a viscosity in the range of 2.500 poises. One of those involved in this development work, M. Pike, then left to join Lorival Ebonite Ltd, where he helped to set their process for DPNR manufacture. The first customer for the Lorival DPNR was Acheson Colloid who required it then and still do today for the inclusion in graphite suspensions.

DPNR production was originally set, however, for the "in-house" manufacture of battery boxes. This firm has always been part of the Chloride Group, a major manufacturer and supplier of batteries both in the UK and abroad. Most battery boxes are now cast using polypropylene; DPNR is only used in the manufacture of the boxes for the largest heavy duty batteries. The firm also supplies polypropylene castings.

A research programme was started in Sri Lanka to develop a commercial process for DPNR manufacture, based on the chemical depolymerisation of rubber using nitrobenzene with solar radiation as the energy source. This project was never taken any further than the trial stage because of problems with the transfer of solar energy to the reaction vessel contents and concern over the project's commercial viability. Trial samples were distributed by "Rubber Convertors" (C.W. Mackie Ltd., Colombo, Sri Lanka).

A research project for DPNR manufacture has recently been started at the Rubber Research Institute of India in response to a request from a local firm (Carborundum , India, Ltd) who currently import 10 tons /year DPNR from Hardman Inc. for use in the manufacture of large grinding wheels. A number of other potential uses for DPNR in India have been identified, including its use as an insulation layer in rocket projectiles and shell casings. This project is proceeding at a very slow pace, mainly because of the lack of suitable equipment. The process being developed is again based on the use of extensive mastication at elevated temperature in the presence of air.

Estimated current world production of DPNR

Following interviews with Chloride Lorival and Hardman Inc. present world production of DPNR is estimated to be

	DPNR production tons /year
Chloride Lorival Ltd	150-200
Hardman Inc	250-300
Total	400-500

At Hardman Inc. there has been a steady but small increase (2% per annum) in demand of DPNR. The same was true at Chloride Lorival until recently. In 1985 there has been a marked increase in demand for DPNR from existing customers and this has meant the introduction of a night shift and recruitment of new staff. Current production levels at both Chloride Lorival

Ltd and Hardman Inc are probably well below installed capacity. Chloride Lorival stated that the current installed capacity is 6-7 tons /week ie an annual capacity of up to 350 tons . However, a significant period of "down time" is necessary to clean the reaction vessels : Chloride Lorival admitted that this was a major problem because, if left unattended, degradation products could build up on the walls of the reaction vessels resulting in a significant drop in the efficiency of the depolymerisation process. Hardman Inc probably have similar problems. Hardman commented very favourably on the clearliness of a LNR sample (produced during trial runs at De Diétrich sample number LNR DD2). Though no samples of the Hardman DPNR were available, it was admitted that the Hardman DPNR was "dirty", presumably due to the presence of thermal degradation products.

Manufacture of synthetic liquid polyisoprene

Only two manufacturers of liquid synthetic isoprene rubber (LIR) were found, Kuraray Isoprene Ltd. (Tokyo, Japan) and Hardman Inc. Hardman Inc manufacture LIR by the same process used for the manufacture of DPNR. The LIR is more expensive than the DPNR because of the high price of synthetic polyisoprene, but despite its high cost a small market for the LIR has been found, estimated to be approximately 50 tons /year (the estimate for LIR manufacturing capacity at Hardman of 1.500 tons /year in Worldwide Rubber Statistics -IISRP- is possibly inaccurate). LIR is used in adhesive formulations in preference to DPNR because of its clarity.

Kuraray manufacture LIR by regulating the polymerisation of isoprene monomer (supplied by Nippon Zeon). Kuraray manufacture a range of LIR's (annexes 3 & 4) and sell approximately 2.000 tons /year in their domestic market and in South East Asia. Sales of the Kuraray LIR in the US have been disappointing, possibly because of its high price (see annex 3) and also agents "targeting" the wrong industries.

Chloride Lorival Ltd also experimented with the manufacture of LIR (by mechanical/oxidative degradation at elevated temperatures of synthetic polyisoprene rubber). Although the product was clean and clear, and its manufacture was easier than DPNR, its high price meant that no market could be found for it.

Marketing

Price and product range :

Chloride Lorival offer a product range of three grades of DPNR (annexes 3 & 4) that differ in their viscosity. In December 1984, the price range of DPNR was £ 2.30-2.90/kg with the lowest viscosity grade the most expensive because of the longer period of mastication required for its manufacture. As a result of the fall in natural rubber prices DPNR prices dropped in mid-1985 to £ 2.00-2.60/kg. Chloride Lorival can supply two part formulations (with room temperature cures) for a number of application (annex 5), but the majority of its DPNR sales are to firms who purchase the DPNR, mainly R25, for use in their own formulations.

Hardman Inc offer five grades of DPNR which also differ in their viscosity (annexes 3 & 4). They can be supplied in two or even three part formulations (with room temperature cures). The majority of sales (annex 5) are for cable filling. As already mentioned, the Hardman range of liquid rubbers includes synthetic LIRs which are used in adhesive formulations, particularly as additives (viscosity modifiers) in pressure-sensitive adhesive formulations.

Both the Chloride Lorival and Hardman product ranges also include liquid (depolymerised) butyl rubbers used in the manufacture of mastics and sealants. Hardman also sell a partially crosslinked butyl rubber (which is not liquid). This product has found considerable acceptance in the sealants industry because its cross-linked (3 dimensional) nature provides a good balance between ease of processing and sag (creep) resistance. Hardman are currently experimenting on producing other liquid synthetic elastomers such as EPDM (for sealing single-ply EPDM roofing).

Kuraray sell a wide range of LIRs (annexes 3 & 4), including chemically modified LIRs. Their price is approximately 20% higher than that of the LIRs sold by Hardman and significantly higher than the price of DPNR. Chemically modified LIRs are also sold including two grades of carboxylated LIR and a partially hydrogenated LIR. These chemically modified LIRs are very expensive but Kuraray are able to sell them in the Far Eastern market, mainly for inclusion in adhesive formulations. Kuraray are expected to introduce more chemically modified LIRs but there is no indications as to what these modifications will be.As far as it could be ascertained no chain extendable LIR has been developed.The high price for the Kuraray LIR should dampen demand for it but approximately 2.000 tons were sold last year (annex 5), mainly in the Far East. One major market (33% of sales) for this LIR is in surgical adhesives were its purity and clarity are important selling points. However, another 600-700 tons were used in the manufacture of tyres. Because of its excellent tack it is used to hold elements of the tyre together before vulcanisation, especially between the steel beads and the rubber.

Marketing :

Industrial sales are achieved by a combination of a number of factors (as perceived by he customer) which, as well as price and physico-chemical properties of the material, would also include continuity of supply, price stability, quality control and technical support. In any examination of the market potential of a new product the marketing methods used are important considerations though rules are always there to be broken. Sheard, in a recent review of the liquid rubber market, suggested that in the future processors will increasingly buy prepackaged compounds or preformulated multi-component systems. The implication is that the rubber processor will concentrate on the manufacture (design and production) and marketing. Technical support and quality control will be entirely provided by the supplier. There is some evidence that the general rubber goods industry is moving in this direction with technical support an important part of the supplier's marketing strategy.

Hardman maintain a sales organisation across the North American continent to develop new sales and to provide the necessary technical support for existing customers. As part of the firm's marketing strategy a broad product range is offered, including two or three part formulations for a wide range of possible applications. A significant proportion of firm's sales is for two part formulations used in applications such as cable filling. Technical support is also provided in the form of information on curing agents, accelerators and antidegradants as well as offering a range of equipment to dispense the liquid rubbers. Outside North America it is sold through agents; in Europe Safic Alcan & Cie and Alcan Italia SpA. This may have limited the firm's ability to penetrate the European markets. Agents dealing with extensive product ranges, often in large volumes, may be unable to provide the sales effort and technical support necessary to promote specialist products sold in comparatively small quantities. As far as the information is available, no Hardman DPNR is sold in the UK, although one firm in West Yorkshire is supplied with 1 ton /year of the liquid butyl rubber.

Kuraray, as part of a major Japanese corporation, are represented abroad by their own trading organisation. Agents also appointed including E.L. Puskas Co. in Akron, Ohio, USA, but with little success so far in the North American continent. Kuraray are planning, however, to expand the market for LIR outside the Far East and have recently installed new manufacturing capacity at their site in Kashima, Japan. At the present time potential markets in Western Europe are being surveyed. In the UK there are two agents , Revertex Ltd. (Harlow, Essex) and Siber Hegner Ltd. (Beckenham, Kent). Siber Hegner survey of the UK market is close to completion survey and is optimistic about LIR's potential especially in the adhesive sector. Other members of the Siber Hegner organisation are carrying out similar market surveys across Europe (Siber Hegner has offices in 11 West European states as well as in Eastern Europe). Revertex was more cautious and expressed concern over the high price of the LIRs.

Chloride Lorival has broken all the marketing rules. Yet despite this, there has been an increase in demand for the firm's LNR. The Chloride group have been in financial difficulties for some time, difficulties that were made very much worse by problems associated with the launch of a new automotive battery in the North American market. As a result of its financial difficulties the Chloride group has been extensively restructured. For Chloride Lorival this happened three years ago when it was decided to concentrate on polypropylene castings and to run down the DPNR side of the business. To achieve this objective, it was decided that whilst DPNR manufacturing capacity would be maintained to supply existing customers, the sales organisation would be disbanded and the salesman made redundant. Despite this, sales of Chloride Lorival DPNR have began to grow appreciably. The end-uses responsible for this increase in demand were not divulged by Chloride Lorival. The firm has been forced however to recruit additional staff so that a new production shift could be introduced. Despite this, there was no evidence that the sales operation would be brought back. In fact it is very difficult to find any references to the firm's DPNR product range and the sale literature for the DPNR product range, provide during a recent visit, was several years old. It seems that despite the improvement in sales, the firm is not committed this part of its business activity.

There are considerable difficulties in achieving significant sales or market penetration without a "dedicated" sales force. The market for liquid elastomers is a special one which is also highly fragmented with a large number of small volume applications. There is also a wide range of alternative synthetic liquid elastomers, all of which are marketed aggressively on both their price and physico-chemical properties. Whilst Hardman has a significant sales operation in the North American continent it does not have one in Western Europe. Discussions at Hardman revealed that the firm is keen to enter the West European market to improve sales growth (and capacity utilisation ?) but without any sales organisation in the West European market sales have been very poor disappointing. During the present investigation almost all the firms contacted were unaware of/or made no comment on the availability of DPNR or LIR from Chloride Lorival, Hardman or Kuraray.

7.2.5.2. The potential market for Liquid Natural Rubber

As mentioned above , the concept of a pumpable and castable DPNR was of consirable interest but, unfortunately, DPNR cannot be used to replace natural rubber. It can be transformed into desired shapes far more easily than natural rubber and then made dimensionally stable by vulcanization, but it has lost most of its rubbery properties and has very poor physical properties (for example low tensile strength). Without reactive terminal groups there is no method currently available to chain extend the depolymerised molecules and recreate the rubbery properties of the original natural rubber.

DPNR should not be seen as a replacement for natural rubber but as a speciality product whose applications make use of its specific properties, for example low viscosity, good low temperature properties, good tack and possible low electrical conductivity. The major proportion of Hardman's sales of DPNR are for cable filling. Encapsulation of low power electrical components is another important end-use. The majority of the DPNR sold by Chloride Lorival is exported to a Dutch firm manufacturing mastics. Chloride Lorival also export DPNR to a dealer in West Germany but the firm did not know what this DPNR is used for. In the UK, DPNR is sold to Acheson Colloid, to ICI for sealing pipework in the Chlor-Alkali plant at Runcorn (the Mond Division) and to other firms manufacturing mastics and adhesives.

The primary use for LIR is in manufacture of adhesives (surgical adhesives and in hot melts) where its clarity and purity give it a considerable marketing advantage over the lower cost DPNRs. Kuraray have also exploited, in the Far East, a significant market for LIR as a tackifier in the tyre industry. This is one market in which DPNR could be successful, especially as it is cheaper than LIR and properties such as clarity are not important. If this Far Eastern market uses 600-700 tons LIR/year worldwide demand could be in the region of 2.500 tons /year. However, this market is likely to be extremely difficult to exploit.

There is a good chance that the new DPNR will be able to displace the older versions in applications such as these : it will not be more expensive (though, as noted) we do not think it will be cheaper, when the marketing and distribution costs are taken into account) and it is a better, cleaner material.

Therefore, given appropriate promotion (the effort and cost of which should not be under-rated), there is a market of around 500 tons /year available for the new DPNR. In order to ensure that the new DPNR is able to achieve this market penetration, we suggest that attention should be paid to two features, in an effort to reduce the selling price : (1) the possibility that a higher molecular weight (and therefore cheaper) DPNR might be adequate for some applications, and (2) investigation of the use of cheaper redox systems.

On this basis, we suggest that one plant with a nominal capacity of about 1.000 tons /year would be large enough to satisfy estimated demand for the time being. A plant of this size, costing about US$ 2 million , would not be likely to be operated at more than 50-60 per cent of capacity in the early years.

7.3. MARGINAL COSTING OF LIQUID NATURAL RUBBER MANUFACTURE

7.3.1. Pilot plant

7.3.1.1. Costing of LNR manufacture

For a pilot plant established at the IRCA-RCI site, Bimbresso, near Abidjan in the Côte d'Ivoire.

7.3.1.2. Fixed capital

In calculating the charge for the capital investment the present value of the salvage price of the plant and machinery has been deducted from the cost of the capital item.

	Cost CFA	Salvage Value %
Pilot plant	80.000.000	20
Building for pilot plant	26.250.000	50
Installation		-
Emergency generator	7.200.000	40
Installation	500.000	-
Truck (car)	4.500.000	written off in 3 years

With regard to the installation of the pilot plant, there were no charges for laying in electricity lines, roads, sewage and drilling for water and erecting a water tower - costs that must be included in the analysis of an industrial production plant. There is also no charge included in this analysis for effluent treatment. The incinerator in use at the present time is hopelessly inefficient. Trials have been started to test the use of an activated charcoal column to remove toxic materials from the effluent stream. If this is successful it will provide a very low cost method for effluent treatment. It may be possible to obtain activated charcoal locally at very low cost using coconut fibre. One possible source would be from fishermen who use coconut husks for smoking fish. The coconut fibre is then placed in a lengh of industrial PVC tubing and the effluent stream passed through it. At the present time the results of the initial trials are not available.

Capital Investment

	CFA
Pilot Plant	80.000.000
Salvage value 20%	16.000 000
Present value of salvage (10% over 10yrs)	6 168 688
Capital to be charged	73.831.312
Building	26.250.000
Salvage value 50%	13.125.000
Present value of salvage (10% over 10yrs)	5 060.252
Capital costs to be charged	21.189.748
Emergency Generator	7.200.000
Salvage value 40%	2.880.000
Present value of salvage (10% over 10yrs)	1.110 364
Capital costs to be charged	6.089.636
Total charge for investment in plant	101.110.696
Installation charges	10.500 000
Total capital charge	111.510.696
Fixed Capital cost per annum (at 10% for 10 years)	18.164.126,25
Charge for car per annum (3 years at 10%)	1.809.516,60
Total charge per annum for capital investment	19.973.642,85

Chemicals

	Cost to IRCA-RCI CFA/kg	In pilot plant kg consumed per 200kg LNR	Cost to CFA per ton LNR produced
Latex	250,0	200,0	250.000,0
Ammonia	435,0	2,3	5.002,5
Sodium hydroxide	281,2	0,4	562,4
Phenyl hydrazine	3.562,5	17,28	307.800,0
Nekal soap	1.500,0	2,0	15.000,0
Antifoam	7.159,5	0,5	17.898,75
Acetic acid	562,5	20,0 litres*	56.250,0
Total			652.513,65

*in experiment 101 acetic acid was found sufficient to coagulate the LNR so cost of acetic acid now becomes	28.125,0
and new total	624.388,65

Contribution of chemicals to total cost of chemicals

	% total cost
Latex	40,0
Ammonia	0,8
Sodium hydroxide	0,1
Phenyl hydrozine	49,3
Nekal soap	2,4
Antifoam	2,9
Acetic acid	4,5
	100,00

Drums

Drums (200l) can be supplied locally though no discounts are available on orders less than 1000 drums (an order size not envisaged though price would be approximately 1200 CFA).

Current price is

per drum	14767 CFA

To paint the internal surface of the drum (approximately 3m^2) requires 0.5kg paint at 2000 CFA/kg

cost per painted drum	15767 CFA
and per 5 drums (for 1 ton)	78835 CFA

Transport

Current cost to transport 1 ton from IRCA-RCI (Bimbresso) to dockside at Abidjan 15.000 CFA/ton

Energy

The pilot plant uses electricity as its sole source of energy drawn from the national supply system.

The tarif structure in February 1983 was

from 06.00 - 18.00 hr.	33	CFA kwh
18.00 - 22.00 hr.	45	CFA kwh
22.00 - 06.00 hr.	27,5	CFA kwh

Because of the present wages and price freeze (that has been in force since 1982), the present tarif structure does not differ. However, for the purposes of the present cost analysis, a figure of 45 CFA per kwh was accepted. A separate analysis of rubber factories in 1983 estimated the cost of electricity as 40+2 CFA per kwh.

At the present level of efficiency the pilot plant requires 2,3 kwh per kg LNR produced ie 460 kwh per 200 kg. However, since electricity supplies cannot be maintained, an emergency generator has been installed. It is assumed that the generator provides 5% of the plant's energy requirements throughout the year.

Average time to produce 200 kg LNR	45 hr
So per 200 kg samples use	2,25 hr generator
At full load the emergency generator assumes	20 litres diesel/hr
Cost of industrial diesel fuel (DDO)	137 CFA/litre
Cost of emergency generator per 200 kg LNR	6165 CFA
Main supply provides	437 kwhr
Cost per kwhr	45 CFA
Cost of mains electricity per 200 kg LNR	19.665 CFA
Total energy cost per 200 kg LNR	25.830 CFA
Energy cost per ton LNR	129.150 CFA

Maintenance charges

For both pilot plant and emergency generator they are calculated to be 7 % for the first 2 years and there after 10 % per annum of original cost.

Total maintenance charge over 10 years

- pilot plant	75.200.000
- emergency generator	6.768.000
	81.968.000
so maintenance cost per annum	8.196.800

Manpower

Current cost of employing staff

- ivorien supervisor	100.000 CFA/week
- staff for plant and effluent treatment	50.000 CFA/month
- laboratory staff	75.000 CFA/month [1]
- secretary	40.000 CFA/month
- driver	40.000 CFA/month

[1] this also includes the charge for laboratory use and laboratory chemicals

manpower requirements for pilot plant at the present time

	number	CFA/year
- staff for plant and effluent treatment	5	3.000.000
- laboratory staff	1,5	1.350.000
- secretary	0,5	240.000
- driver	0,5	270.000
		4.860.000

So manpower cost for 1 ton :

at production 10 tons	a year	486.000 CFA
and production 20 tons	a year	243.000 CFA

MANUFACTURING COST FOR 1 TON OF LNR

capacity utilisation	50%		100%
LNR, ton /year	10		20
		CFA	
Chemicals		624.389	
Energy		129.150	
Drums		78.835	
Transport		15.000	
		847.374	
Capital charges	2.498.044		1 249.022
Manpower	486.000		243.000
Maintainance	814.660		407.340
	4.646.098		2.746.736
(or	Fr92.922		Fr54935)
Working capital			
10% of chemicals including latex	624.389		1 248.776
10% of annual production	4.646.098		5.493 472
	5.270.487		6.742 248
per ton LNR	527.049		674.225
TOTAL COST (CFA)/TON LNR	5.173.147		3 420 961
(or	Fr103.463		Fr68.419)

7.3.2. Industrial plant

7.3.2.1. Chemicals

From the analysis of pilot plant, the cost of the chemicals including latex is 624.388 CFA (12,1 - 18,3 % of the total manufacturing costs depending on capacity utilisation). The chemicals accounting for the major share of these costs are :

- phenylhydrazine	49,3 %
- field latex	40 %

Phenylhydrazine

The phenylhydrazine is supplied by Hoescht, from West Germany through their agent in Abidjan, and its price is 2.850.000 CFA/ton (excluding tax). Tax for chemicals imported into the Côte d'Ivoire is 85 % of their factory gate price. However, for imported goods required for the rubber industry the rate of taxation is reduced to 25 %. Present demand for phenylhydrazine is 1-2 tons per annum. If production of LNR is increased to 1.300 tons per annum, demand for phenylhydrazine will be between 100-150 tons per annum (which at current prices would be worth over £ 0,5 million to Hoescht). It should be possible to obtain a discount on the present price of phenylhydrazine. Hoescht claim that their price structure is very shallow with maximum discounts obtained for small order quantities. If a 10 % price reduction was achieved then the price of phenylhydrazine would become 2.565 CFA/kg and in the Côte d'Ivoire, after import duty/tax, 3.206,25 CFA/kg. Production of 1 ton LNR with a viscosity 368.000 cps (at 25°C, Mv 10.000) requires 86,4 kg phenylhydrazine costing 277.020 CFA. The best selling grade of LNR supplied by chloride Lorival is R25 with a viscosity of 25.000 poises (at 23°C, MW = 23.000). Manufacture of an equivalent grade of LNR would require 50 % less phenylhydrazine which would then cost 138.510 CFA.

Latex

For calculating the cost of manufacturing LNR using the pilot plant the price of field latex was taken as the average selling price of latex. Since LNR manufacturing plant would be closely associated with a rubber plantation/factory the price of field latex charged to the manufacture of LNR would be much closer to the cost of harvesting the latex. The cost of producing latex in the Côte d'Ivoire is not known. If a 10 % reduction in the cost of field latex was achieved the cost of latex per one ton LNR produced would become 225.000 CFA.

7.3.2.2. Drums

Because of the number of drums (maximum number 6.500) required for storage and transport of the LNR (annually 1.300 tons) discounts will be available.

For 5 drums (required for 1 ton LNR)		60.000 CFA
Paint for 5 drums		5.000 CFA
	total	65.000 CFA/ton LNR

The reuse of drums has not considered in this calculation; it is unlikely that the reuse of drums would bring about any substantial reductions in the manufacturing costs.

7.3.2.3. Transport

There is no evidence whether quantity discounts are available on the costs to transport LNR to the dock at Abidjan. If a 10 % reduction was achieved cost of transport would become :

13.500 CFA/ton LNR

7.3.2.4. Energy costs

Energy consumption by the pilot plant was calculated to be 2,3 kWh/kg LNR produced. Estimates for the industrial plant, with production capacity 1.300 tons LNR per annum, utilising the new thin layer drying technology indicate energy consumption of 2,1 kWh/kg made up of 1,8 kWh/kg for operating the reaction vessels and drier and 0,2 kWh/kg for ancillary equipment. For the purposes of this calculation this will be considered as a 10 % saving in energy consumption and assuming utilisation of the emergency generator follow a similar pattern to the pilot plant;

energy cost 116.235 CFA/tons LNR

(there is no reduction in energy consumption to manufacture the higher viscosity grades of LNR).

Capital expenditure

Field latex collection

A plant with capacity for 25 tons /week (1.300 tons per annum) will require 85 m^3 field latex per week or 17 m^3 field latex per day (assuming a 5 day week for collecting latex). Stainless steel tanks have to be used to collect the latex because of the ammonia added to stabilize the latex. Stainless steel tanks available hold 1,2 m^3 so to fullfill production requirements 14-15 full tank loads of latex have to be delivered each day. One tractor can haul 3 tanks so estimated requirements are :

2 tractors	at	7.000.000 CFA each
6 tanks	at	1.865.000 CFA each

Plant will also require use of 1 small car which has an average working life of 3 years

1 car at 4.500.000 CFA.

Plant

The industrial plant proposed by De Diétrich incorporates a new continuous "thin-film" drier to replace the batch vacuum drier used in the pilot plant. Otherwise the design of the plant is the same used for the pilot plant.

Estimated cost of plant 13,5 millions FFr
or 675.000.000 CFA

(this price excludes the cost of transport/installation).

Buildings : the building to house the plant must have a minimum height of 20 metres for installation of the drying equipment.

Building for production plant	50.000.000 CFA
Building for storage of chemicals/drums, etc	30.000.000 CFA
Emergency generator	10.000.000 CFA

Installation : no complete estimates are available of costs to construct building and install plant, emergency generator or equipment for effluent treatment; estimates available

locate and drill for water	4-6.000.000 CFA
construction of water tower	?

install transformer	7.000.000 CFA
lay in power lines from national grid	?
install emergency generator	1.000.000 CFA
to provide road access	?
to provide drains , etc	?

for the purpose of this calculation installation costs are estimated to be 10 % of capital investment.

Capital investment	is	765 millions CFA
so assumed installation cost	is	80 millions CFA

Salvage value of capital equipment

	% of cost price
manufacturing plant	20
buildings	50
generator	40
tractors	none
steel tanks	50
car	none

Salvage value of plant and machinery

	CFA
Manufacturing plant	675.000.000
salvage 20%	135.000.000
present value of salvage (at 10% for 10 years)	52.048.305
so charge for plant	622.951.695
Buildings	80.000.000
salvage 50%	40.000.000
present value of salvage (at 10% for 10 years)	15.421.720
so charge for buildings	64.578,280
Generator	10.000.000
salvage 40%	4.000.000
present value of salvage (at 10% for 10 years)	1.542.172
so charge for generator	8.457.828
Tractor (2 off)	14.000.000
no salvage value	
Steel Tanks (6 off)	11.190.000
salvage 50%	5.595.000
present value of salvage (at 10% for 10 years)	2.157.113
so charge for steel tanks	9.032.887
Car	4.500.000
lifetime 3 years (see calculation for pilot plant)	

Capital equipment

	Charge CFA	Cost of capital at 10% for 10 years
Plant	622.951.695	101.382.516,60
Buildings	64.578.280	10.509.817,36
Generator	8.457.828	1.376.472,52
Tractors	14.000.000	2.278.435,46
Steel tanks	9.032.887	1.470.060,72
Car	4.500.000	1.809.516,60
Cost of investment per annum in plant and machinery		118.826.819,26

Installation

Cost for installing all the plant and machinery is assumed to be 80.000.000 CFA, then

Cost of capital for installation (at 10% for 10 years)	13.019.631,20
Total charge per annum for capital investment	131.846.450,46

Maintenance and running costs

For plant and generator estimated to be 7% for the first 2 years and then 10% per annum for the next 8 years. For buildings assume maintenance costs are 5% of capital cost.

	Capital cost CFA	Total maintenance cost CFA	Maintenance cost per annum CFA
Plant	675.000.000	634.500.000	63.450.000
Generator	10.000.000	9.400.000	940.000
Building	80.000.000	40.000.000	4.000.000
Tractor	14.000.000		2.542.800
Car	4.500.000		1.000.000
Total cost of maintenance per annum			69.390.000
Cost of capital investment per annum			131.846.450
Total cost of capital expenditure per annum			201.236.450

Manpower

From discussions with the designers of the industrial plant it was concluded that at maximum capacity utilisation the plant would require :

	Cost to the employer CFA
3 shifts or 3 operators	50.000/month
also required :	
2 supervisors	100.000/month
laboratory support for quality control	
2 technicians	75.000/month
2 drivers	45.000/month
1 secretary	40.000/month

So manpower costs will be :	CFA/year
9 operators	5.400.000
2 supervisors	10.400.000
2 laboratory technicians	1.800.000
2 drivers	1.080.000
1 secretary	480.000
Total labour cost per annum	19.160.000

Manufacturing costs for an industrial plant producing 1.300 tons LNR/year

<table>
<tr><th></th><th colspan="2">CFA/ton LNR</th></tr>
<tr><th></th><th>Mv 10.000</th><th>Mv 20.000</th></tr>
<tr><td>Chemicals</td><td>568.608</td><td>430.098</td></tr>
<tr><td>Drums</td><td>65.000</td><td>65.000</td></tr>
<tr><td>Transport</td><td>13.500</td><td>13.500</td></tr>
<tr><td>Energy</td><td>116.235</td><td>116.235</td></tr>
<tr><td></td><td>763.343</td><td>624.833</td></tr>
<tr><td>Cost of capital and maintenance</td><td colspan="2">201.236.450</td></tr>
<tr><td>Manpower</td><td colspan="2">19.160.000</td></tr>
<tr><td></td><td colspan="2">220.396.450</td></tr>
<tr><td></td><td>MV 10.000</td><td>MV 20.000</td></tr>
<tr><td>Cost per ton</td><td colspan="2">169.536</td></tr>
<tr><td>Manufacturing costs</td><td>932.879</td><td>794.369</td></tr>
<tr><td></td><td>(or Fr. 18.658</td><td>and 15.887)</td></tr>
</table>

Working capital

This is calculated as the sum of 10% of the value of annual chemical inputs (including latex) and 10% of the value of the plant's annual production (1.300 tons LNR) spread over the year production.

These figures are for the low viscosity LNR.

Chemical inputs	130 tons	x 568.608 CFA/tons	= 73.919.040 CFA
Production	130 tons	x 932.879 CFA/tons	= 121.274.270 CFA
and diesel fuel, require 5% estimated annual consumption (using the figures for the pilot plant (137 CFA/litre and 5% of annual consumption is 2.925 litres)			= 400.725 CFA
			195.594.035 CFA/year

so working capital for low viscosity LNR is 150.457 CFA/ton

the working capital for the high viscosity LNR (calculated on the same basis as the low viscosity LNR)

high viscosity LNR is 122.755 CFA/ton LNR

PRODUCTION COSTS FOR LNR MANUFACTURE

	low viscosity LNR (Mv 10.000) CFA	high viscosity LNR (Mv 20.000) CFA
Manufacturing costs	932.879	794.369
Working capital	150.457	122.755
CFA/tonne LNR	1.083.336	917.124
	(or Fr. 21.667	and 18.342)

Note

Contribution of working capital to production costs can be adjusted to suit (i) prevailing conditions, ie reduced if less capital is tied up because supplies can be obtained without delay or product is shipped out regularly, and outstanding debts are kept to a minimum (ii) by changes in product mix, ie if more high viscosity LNR was manufactured working capital requirements could be reduced since the amount of capital tied up in chemical stocks or products is smaller (see below).

Analysis of production costs/sensitivity analysis

	low viscosity LNR		high viscosity LNR	
	CFA	%	CFA	%
latex	225.000	20,8	225.000	24,5
chemicals	343.608	31,7	205.098	22,4
(of which phenylhydrazine	277.020	25,6	138.510	15,1)
drums and transport	78.500	7,2	78.500	8,6
energy	116.235	10,7	116.235	12,7
labour	14.738	1,4	14.738	1,6
capital				
(i) investment	101.420	9,4	101.420	11,1
(ii) maintenance	53.377	4,9	53.377	5,8
(iii) working	150.457	13,9	122.755	13,4

This sensitivity analysis of the LNR production costs gives us a picture of the contribution the various components of the manufacturing process make to the overall cost of manufacturing LNR and how changes in the cost of these components alter the final production cost. For example, 50% less phenylhydrazine is required to produce the high viscosity LNR. The sensitivity analysis of the production costs shows that a 1% reduction in the cost of phenylhydrazine will lower the production cost for low viscosity LNR by 0,256%. So a 50% reduction in the cost of the phenylhydrazine input will lower production costs by 12,8% from 1.083 CFA/ton to 944.669 CFA/ton . The difference between this figure and the calculated production cost of 917.124 CFA/ton for the high viscosity LNR is accounted for by the reduction in working capital provision (since phenylhydrazine stocks can be reduced less capital is tied up in stockholdings).

This analysis identifies latex (20,8%) and phenylhydrazine (25,6%) as the principal costs in the manufacture of low viscosity LNR. Capital (working capital 13,9% and investment capital 9,4%) and energy (10,7%) are the other major costs. Efforts to minimise production costs should on the basis of this analysis examine ways to reduce the cost of latex and phenylhydrazine. Futher savings could be achieved by obtaining low cost investment capital and possibly by adjustments in working capital requirements to suit prevailing conditions (note that working capital could also be a source of revenue). When high viscosity LNR is produced (requiring 50% less phenylhydrazine) working capital is marginally lowered to 13,4% of the production costs (because of reductions in stockholding requirements and cheaper product) whilst the contributions from latex (24,5%), energy (12,7%) and investment capital (11,1%) all increase.

These calculations were made on the basis of 100% capacity utilisation with return on investment (ROI) 10% over 10 years, both probably unrealistic assumptions. Production costs for both low and high viscosity LNRs calculated on the basis of ROI 15% over 10 years for different levels of capacity utilisation now become,

% Capacity utilisation	Production costs Fr/tonne	
	Low viscosity	High viscosity
100	23.029	19.705
90	23.594	20.270
80	24.302	20.977
70	25.211	21.887
60	26.423	23.099
50	28.120	24.796
40	30.666	27.342

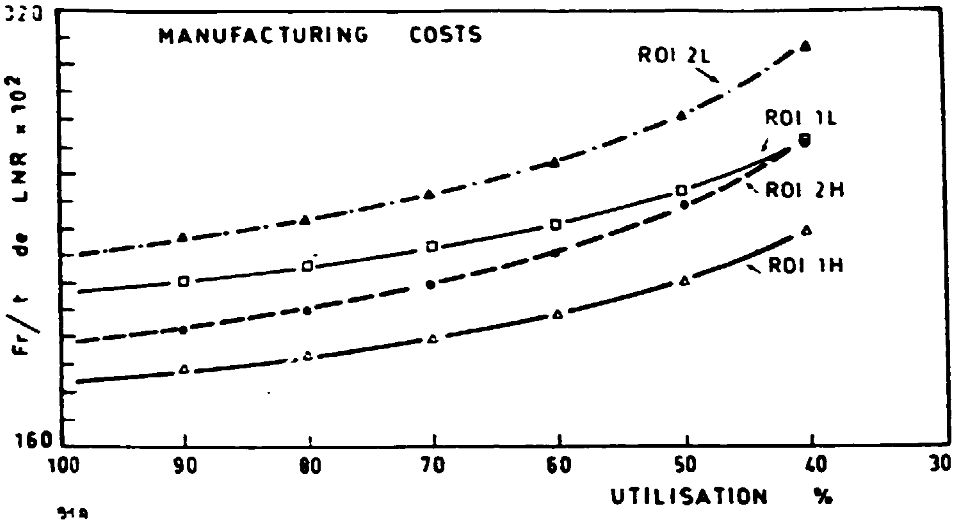
(ROI 15% over 6 years)

These figures demonstrate (see figure 7.1) the effect of low capacity utilisation on production costs which increase at a faster rate as capacity utilisation decreases. Figure 7.1 also illustrates the effect of cost of capital on production costs for changes in capacity utilisation. As the cost of capital increases there is a proportionally greater increase in production costs with decreasing capacity utilisation; changes in fixed costs such as the cost of chemicals cannot alter the shape of this curve. The data for figure 7.1 can be found in Annex 6.

To summarise, the effect of decreasing capacity utilisation is to increase the cost of the capital investment as a proportion of the total production costs and this increase becomes greater as the cost of capital increases. Other costs such as working capital and chemical decrease slighty as a proportion of the final cost with decreasing capacity utilisation (the data illustrating these points can be found in Annex 7.

Conclusions from this analysis of production costs

(1) match plant capacity with the readily available market size; it may be more cost effective to add additional capacity when required instead of opperating inefficiently at low capacity utilisation
(2) minimise the cost of phenylhydrazine and latex
(3) seek the "cheapest" investment capital
(4) minimise working capital requirements; for example, minimise stockholdings of chemicals particularly phenylhydrazine (which can otherwise tie up a considerable amount of capital) as well as the usual methods to reduce working capital by minimising debts and obtaining favourable credit terms.



	Return on Investment (ROI)	LNR Viscosity
ROI 1 L	10% over 10 years	Low
ROI 1 H	10% over 10 years	High
ROI 2 L	15% over 6 years	Low
ROI 2 H	15% over 6 years	High

Figure 7.1

The effect of cost of capital on manufacuring costs when capacity utilisation changes

CHAPTER - 9

CONCLUSION

During this contract "Development of Liquid Natural Rubber", a process allowing LNR to be obtained from field latex has been successfully transposed from the laboratory to the industrial stage.

The pilot unit which works very satisfactorily in the Côte d'Ivoire has been designed so that the incidence of several parameters can be studied without any risk, making it possible to control the depolymerization reaction and obtain a range of LNR with variable but controlled viscosimetric weights varying from $\overline{Mv}$ 7,500 to $\overline{Mv}$ 25,000.

The very high price of phenylhydrazine in the present market conditions plays a major role in the final cost of LNR. A developed production of LNR in larger and more regular amounts will necessarily decrease the selling price of phenylhydrazine, owing to an increase in its consumption. The adjustment of operating conditions - depolymerization in the presence of pure oxygen or under pressure, addition of chemical products stabilizing rubber viscosity or short stoppers - could not be examined enough owing to the short period of time available between the starting of the pilot plant and the end of the contract. This study should be continued in order to reduce as much as possible the amount of phenylhydrazine to add at the beginning of the reaction.

Without any industrial experience on the behaviour of LNR, it was not wise to apply drying techniques more sophisticated but also more efficient than the simple and reliable but energy-consuming process that is currently used. Now that the process of LNR preparation is properly mastered, a thin layer continuous dryer seems well-adapted for the drying of latex coagulum from depolymerized rubber. The LNR obtained by the process developed in the Côte d' Ivoire is of a fine appearance and of a quality estimated higher than that of the rubber obtained by mechanical-chemical depolymerization. The physico-chemical properties of the product obtained in the pilot plant correspond to those determined at the beginning of the contract. The fact low molecular weights are easily obtained is of a great industrial interest and one of the assets of the current process.

The objective aimed at in the development of presentations of natural rubber in liquid form is to offer it new market shares reserved so far for synthetic rubbers. Two approaches have been explored during this contract : identification of non modified LNR market and study of LNR chemical modification to develop products with a higher value added.

The crisis hitting the industry in general and especially the rubber industry has hampered the efficient development of LNR. It took a very long time for manufacturers to answer and several, often the most interested, have not finished their laboratory trials.

Consequently, apart from the market share identified for LNR obtained by mechanical-chemical degradation, that is 500 tons /year, it is difficult to know exactly the volume or extent of other potential markets especially since, as the uses LNR is destined to are often very technical, the users do not wish to divulge the use they think of.

Thanks to chlorine and maleic anhydrid chemical modification of LNR, carried out in the laboratory, it is possible to obtain products, especially chlorinated rubber, the interest of which would justify the development of a production in a pre-pilot unit with a view to an industrial development.

Epoxydation of latex of depolymerized natural rubber is achieved in conditions that are identical or even easier than those of latex of high molecular weight rubber. It leads to a wide range of products, some of which will find outlets especially in the adhesive industry.

Each type of modified rubber mentioned above is the first step to the development from natural rubber, of more elaborated products called "second generation" products which should find applications in many fields. Organic chemistry supplies thus a great contribution to the valorization of a natural and therefore renewable raw material.

Natural rubber producing countries wish, with just cause, to develop their own rubber processing industry to give an increased value to this strategic raw material. Heavy investments therefore are necessary to acquire foreign equipment and technology. The success of such a contract or the previous ones carried out by other IRRDB member institutes, development of thermoplastic and composite rubbers for instance, are an efficient complement, by the development of new forms of rubber, to the transfer of technology from industrialized countries to developing countries.

CHAPTER - 9

LIQUID NATURAL RUBBER - WORKSHOP

ABIDJAN 20-24 JANUARY 1986

A Workshop took place in Abidjan from the 20th to 24th of January 1986, joining experts of UNIDO and of the Institutes members of IRRDB, Germany Federal Republic representatives, as well as a representative of the Ministry of National Education and Scientific Research and of the Ministry of Industry.

In course of this Workshop, the main results achieved during the contract duration have been submitted, as well as others statements concerning different manufacturing process of liquid rubber and overviews of the rubber industry in some countries members of IRRDB, according to the undermentioned programme.

WORKSHOP PROGRAMME

Monday 20th January, 1986 - morning

Conference official opening in presence of the National Education and Scientific Research Minister, Dr. Balla Keita, the authorities of Côte d'Ivoire, the UNIDO, R.F.A. and IRRDB representatives.

\- afternoon

IRCA-IRAP - Mr. Boccaccio and Pr. Brosse
"Parameters of LNR depolymerisation reaction"

IRCA - Mr. Sainte-Beuve
"Description and operating principle of the LNR production pilot plant"

IRCA - MMrs. Allet-Don & Lemoine
"LNR production by the pilot plant in Côte d'Ivoire"

Tuesday 21st January, 1986 - morning

IRCA-IRAP - Mr. Marteau
"Potential applications of LNR"

MRPRA - Dr. Bristow
"Some possible new applications of LNR"

MRPRA - Dr. Allen
"Economic aspects of LNR : production and markets"

- afternoon

RRI - Dr. Tillekeratne
Sri Lanka "Manufacture of liquid rubber from crepe rubber using solar radiations"

GFR - Dr. Nordsiek * Hüls Aktiengesellschaft
"Liquid rubber technology based on butadiene polymers"

SAPH
Côte d'Ivoire
- Mr. Bille
"Overview of the heveaculture in Côte d'Ivoire"

BPPB - Dr. Budiman
Indonesia "Prospects of domestic rubber usage in Indonesia"

Wednesday 22nd January, 1986

Day in IRCA - Visit and presentation of the operational pilot plant - visit of the plantation.

Thursday 23rd January, 1986 - morning

SCATC - Dr. Mei Tongxian
China "Some views on the development of liquid natural rubber in China"

IRCA-IRAP- Mr. Boccaccio
"Liquid natural rubber, chlorine and maleic anhydrid chemical modifications"

IRCA-IRAP- Pr. Brosse
"Liquid natural rubber, present situation and prospects"

- afternoon

Closing session in presence of the Côte d'Ivoire National Education and Scientific Research Minister, Dr. Balla Keita, the Austrian and German Ambassadors, the UNIDO and IRRDB representatives.

Friday 24th January, 1986 - morning

Visit of a rubber estate.

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* Dr. Nordsiek couldn't attent to the Workshop; some elements of his lecture will be given in the proceedings.

WORKSHOP COMMITTEE

UNIDO representatives

Mr. YOUSSEF
Dr. MULLINS

UNIDO experts

Dr. S. BUDIMAN	BPPB Indonesia
Dr. LMK TILLEKERATNE	RRI Sri Lanka
Dr. GM BRISTOW	MRPRA
Dr. PW ALLEN	MRPRA
Dr. BROSSE	Université du Maine France
Mr. MEI TONGXIAN	SCATC China
Mr. CHEN XI XIN	SCATC China
Mr. ZAINAL BIN MAIDUNNY	RRIM Malaisia
Miss NEVES	EMBRAPA Brazil
Mr. SURASAK SUTTISONG	RRC Thailand

IRRDB experts

Mr. de PADIRAC	IRRDB-IRCA
Mr. de LIVONNIERE	IRCA France
Mr. BANCHI	IRCA Côte d'Ivoire
Mr. LAIGNEAU	IRCA Côte d'Ivoire
Mr. SAINTE BEUVE	IRCA Côte d'Ivoire
Mr. LEMOINE	IRCA Côte d'Ivoire
Mr. ALLET DON	IRCA Côte d'Ivoire
Mr. BOCCACCIO	IRCA-IRAP France
Mr. MARTEAU	IRCA-IRAP France
Mr. CARLOS MONTANO	SUDHEVEA Brazil
Mr. NKOUONKAM	IRA Cameroon
Mr. LIU ZÚTANG	SCATC China
Mr. KURIAKOSE	RRI India
Mr. TRAN THAN LONG	IRCV Vietnam

WEBER ET SCHAER GFR

Mr. HOFFMANN

Ministry of Industry

Mr. CHARRA	Côte d'Ivoire

Conclusions and recommendations after the Workshop

1 - It was unanimously agreed by the representatives of the IRRDB member institutes attending the Conference that the project on Liquid Natural Rubber (LNR) which had been implemented by UNIDO and financed by a special purpose contribution from the Government of the Federal Republic of Germany to the UNIDF has successfully achieved its objectives.

2 - A method had been developed to produce LNR from field latex, and a pilot plant had been constructed by IRCA in the Côte d'Ivoire. This is now producing regular supplies of LNR. It has demonstrated that LNR can be produced on an industrial scale using field latex, and he has provided sufficiently large quantities of LNR for a technical and economic appraisal of its commercial potential to be undertaken by potential industrial customers.

3 - Although other IRRDB member institutes have been investigating the possible production of LNR using other forms of natural rubber and other chemical and physical processes. The IRCA process is to date the only feasible process for the production of LNR for inside-scale industrial use. However the use of phenylhydrazine as a reagent in the depolymerization process adds considerably to the cost of the product and the use of an alternative cheaper reagent is urgently required.

4 - The project has shown that there is already a market of about 500 tons a year for LNR and that this market could rapidly increase to about 1.000 tons a year. A number of large international rubber companies have shown great interest in the use of LNR provided that these was a substantial and guaranteed supply. It is therefore recommended that a commercial and economically viable plant should be set-up with a capacity of about 1.000 tons a year.

5 - Laboratory investigations have been carried on the chemical modification of LNR using chlorine, maleic anhydrid, epoxydation and other chemical groups. There is a potential and significant market for such modified materials. Further work on a pilot plant scale is now necessary to enable the processes and the markets to be more fully evaluated. This would be undertaken in Phase II on the project which has already been submitted to UNIDO. UNIDO is requested to look into the immediate implementation of Phase II of the project so as to keep the momentum going and importantly to keep the team together.

6 - All of the natural rubber producing are developing countries actually seeking to expand their rubber products manufacturing industry using locally produced rubber and so adding value to the raw rubber which they produce. But they do not pocesses the large industrial rubber processing plants which require heavy investment and are still typical of the industrialized countries. However, in these times of rapide change involving the use of more highly automated machinery, this is an opportunity for the developing countries to "leap from" existing technology and with close cooperation between producers and consumers to adopt most modern techniques using LNR in special and automated equipment which takes full advantage of the new form. This would also provide a sound base for exports of LNR as the new technology becomes more widely adopted throughout the world.

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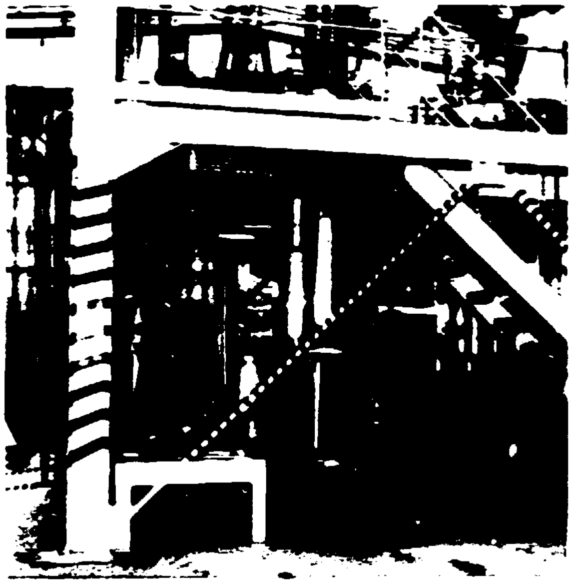

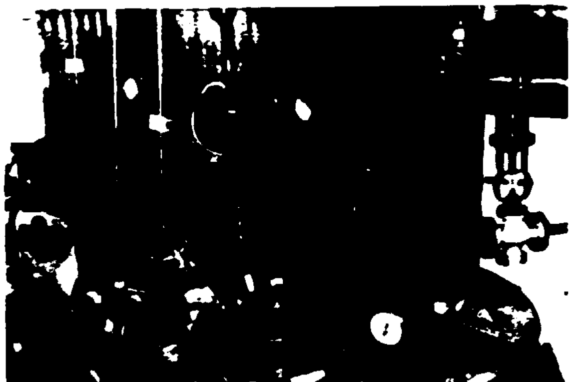

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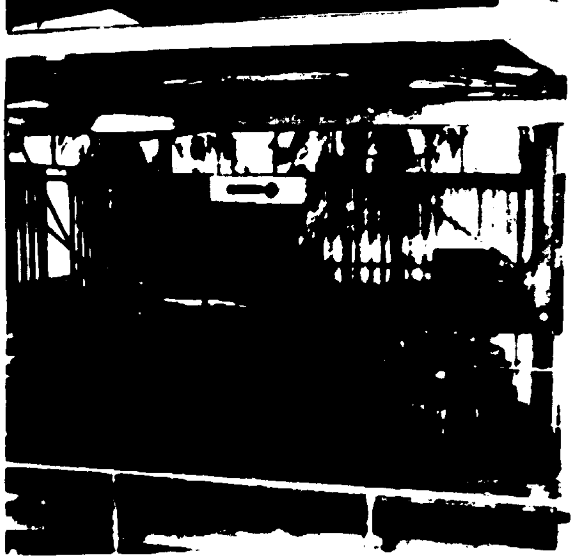

ANNEX 2

Current Prices of Liquid Elastomers (August, 1985)

		£/kg	price as % of the price of Lorival LNR (£2.15/kg)
Polybutadiene	unsaturated	1.55	72
	unsaturated	2.65	123
	modified	4.00	186
	-COOH terminated	11.78	548
SBR		-	-
Butyl	Lorival high* viscosity	3.34	155
	low* viscosity	3.77	175
	Hardman 800	1.70	79
	1300	1.75	81
Nitrile	-COOH	4.33	201
	-SH teminated	4.60	214
Polysulphide		3.455	160
Polychloroprene		2.85	132
Silicone		6 - 170	280-7500
Urethanes			
LIR	Hardman	2.23	103
	Kuraray	2.79	129
	carboxylated	5.09	236
	hydrogenated	3.12	145
DPNR	Lorival	2.15	"100"
	Hardman	1.86	87
NR	RRSI	.6325	29
	SMR 20	.5415	25
	SMR CV	.6475	30

* Hardman also supply these liquid butyl rubbers in low viscosity grades but these preparations contain only 70% rubber solids.

ANNEX 3

Current Prices for DPNR and LIR (November, 1985)

(1) Chloride Lorival Ltd.[1]				£/kg
DPNR	R 5			2.55
	R 25			2.08
	R 200			2.23
(2) Hardman Inc.[1]		$/lb		
DPNR	DPR 01	1.50		2.30
	DPR 400	1.17		1.79
	DPR 75	1.21		1.85
	DPR 40	1.23		1.88
	DPR 35	1.26		1.93
LIR	Isolene 400	1.41		2.15
	Isolene 75		Discontinued	
	Isolene 40	1.51		2.31
(3) Kuraray Ltd.[2]		Yen/kg		
LIR	KLIR 30	850		2.79
	KLIR 50	850		2.79
carboxylated				
	KLIR 403	?		?
	KLIR 410	1550		5.09
hydrogenated				
	KLIR 290	950		3.12

[1] prices ex-factory
[2] prices FOB

ANNEX 4

Properties of DPNR and LIR

		Viscosity	Molecular Weight	
(1) DPNR				
		poises @ 23°C		
Lorival	R5	5 000	13 500	
	R25	23 000	23 000	
	R200	200 000	52 000	
		poises @ 38°C	Mw(GPC)	
Hardman	DPR 01	semi-solid	155 000	
	DPR 400	3 000 - 5 000	80 000	
	DPR 75	550 - 950	45 000	
	DPR 40	340 - 560	40 000	
	DPR 35	300 - 360	38 000	
		poises @ 23°C	Mw(GPC)	
LNR (Côte d'Ivoire)		7 000	33 000	
(2) LIR				
		poises @ 38°C	Mw(GPC)	
Hardman	Isolene 400	3 000 - 5 000	90 000	
	75	550 - 950	45 000	
	40	360 - 550	40 000	
		poises @ 38°C	Mv	Iodine value*
Kuraray	KLIR 30	740	29 000	368
	KLIR 50	4 800	47 000	368
	carboxylated KLIR 403	980	25 000	368
	KLIR 410	1 800	25 000	368
	hydrogenated KLIR 290	10 000	25 000	40

* g/100

ANNEX 5

Applications for DPNR and LIR proposed by manufacturers

DPNR

1. Chloride Lorival

(i) reactive non-extracable plasticiser
(ii) reactive binder for abrasive and friction products
(iii) suspension medium in solutions, greases and lubricants
(iv) useful masterbatch for fine powders
(v) manufacture of flexible moulds and prototype rubber articles
(vi) electical potting compound

2. Hardman

(i) a reactive binder for abrasive and friction products
(ii) a rheology modifier for lubricants and oils
(iii) a vehicle for dispersion
(iv) a rubber processing aid
(v) an asphalt modifier
(vi) an elastomer base for cold moulding compounds
(vii) an elastomer base for electrical potting compounds
(viii) an elastomer base for sealants

LIR

3. Hardman

(i) adhesives; solvent emulsion & hot melt forms

4. Kuraray

(i) reactive plasticiser for tyres, belts and footwear
(ii) adhesives
(iii) pressure-sensitive adhesives
(iv) sealants
(v) modifying agent of adhesive properties of elastomers to metal
(vi) raw materials for chemical modifying reactions

and hydrogenated LIR

(i) reactive modifier of elastomers (EPDM & Butyl rubber)
(ii) modifier of plastics
(iii) hot melt adhesives (SIS, SEBS, EVA)
(iv) raw materials for chemical modifying reactions

ANNEX 6

(1) ROI 10% over 10 years

% Capacity Utilisation	Production Costs Fr/ton	
	Low Viscosity	High Viscosity
100	21 667	18 342
90	22 081	18 757
80	22 606	19 275
70	23 315	19 941
60	24 153	20 829
50	25 396	22 072
40	27 261	2[illegible] [illegible]37

(2) ROI 15% over 6 years

% Capacity Utilisation	Production Costs Fr/ton	
	Low Viscosity	High Viscosity
100	23 029	19 705
90	23 594	20 270
80	24 302	20 977
70	25 211	21 887
60	26 423	23 099
50	28 120	24 796
40	30 666	27 342

ANNEX 7

The Cost of Capital and Chemical Inputs as a Proportion of the Final Production Cost at different Levels of Capacity Utilisation.

	% capacity utilisation	cost as % of total production cost low viscosity	INP high viscosity
CAPITAL			
(1) Investment Capital			
ROI 10% over 10 years			
	100	8.4	10.0
	60	12.6	14.6
	40	16.8	19.1
ROI 15% over 6 years			
	100	12.6	14.9
	60	18.6	21.2
	40	24.0	26.9
(2) Working Capital			
ROI 10% over 10 years			
	100	13.9	13.4
	60	13.4	12.9
	40	12.9	12.4
ROI 15% over 6 years			
	100	13.6	13.1
	60	13.0	12.5
	40	12.5	11.9
CHEMICALS			
(3) Phenyl Hydrazine			
ROI 10% over 10 years			
	100	25.6	15.1
	60	22.9	13.3
	40	20.3	11.6
ROI 15% over 6 years			
	100	24.1	15.1
	60	21.0	13.3
	40	18.1	11.6
(4) Latex			
ROI 10% over 10 years			
	100	20.8	24.3
	60	18.6	21.6
	40	16.3	18.9
ROI 15% over 6 years			
	100	19.5	22.8
	60	17.0	19.3
	40	14.7	16.3

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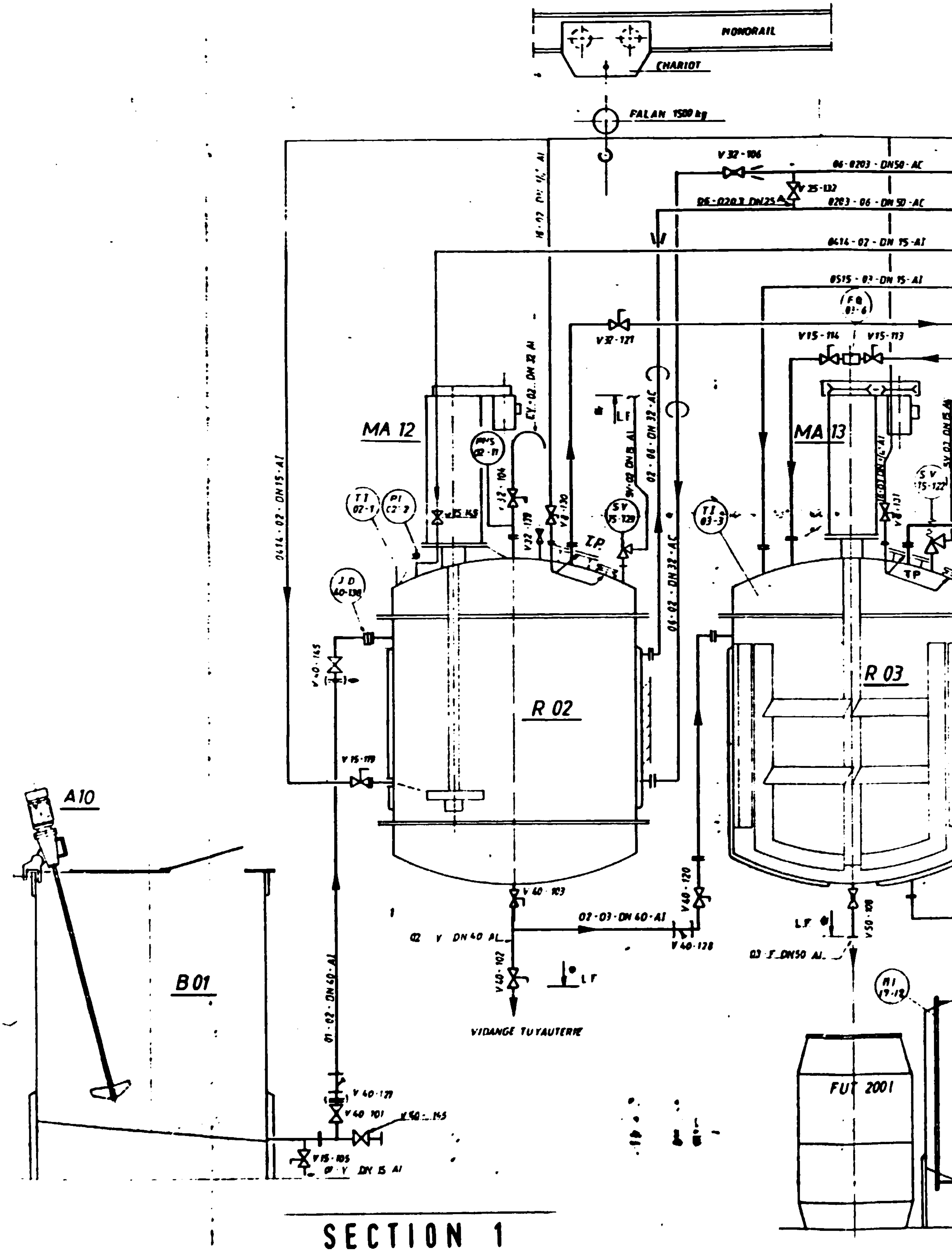
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CHARIOT
FALAN 1500 kg
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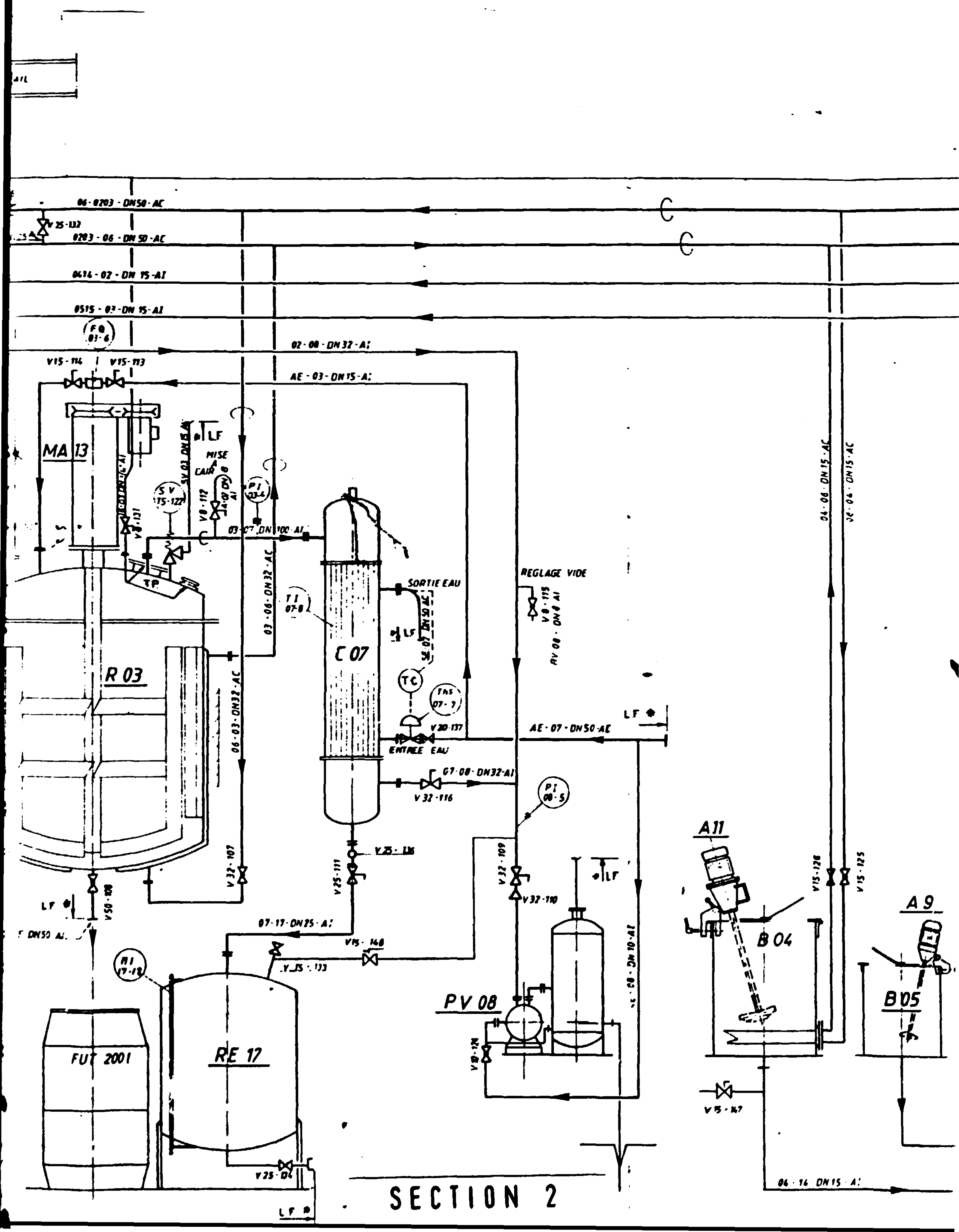
SECTION 1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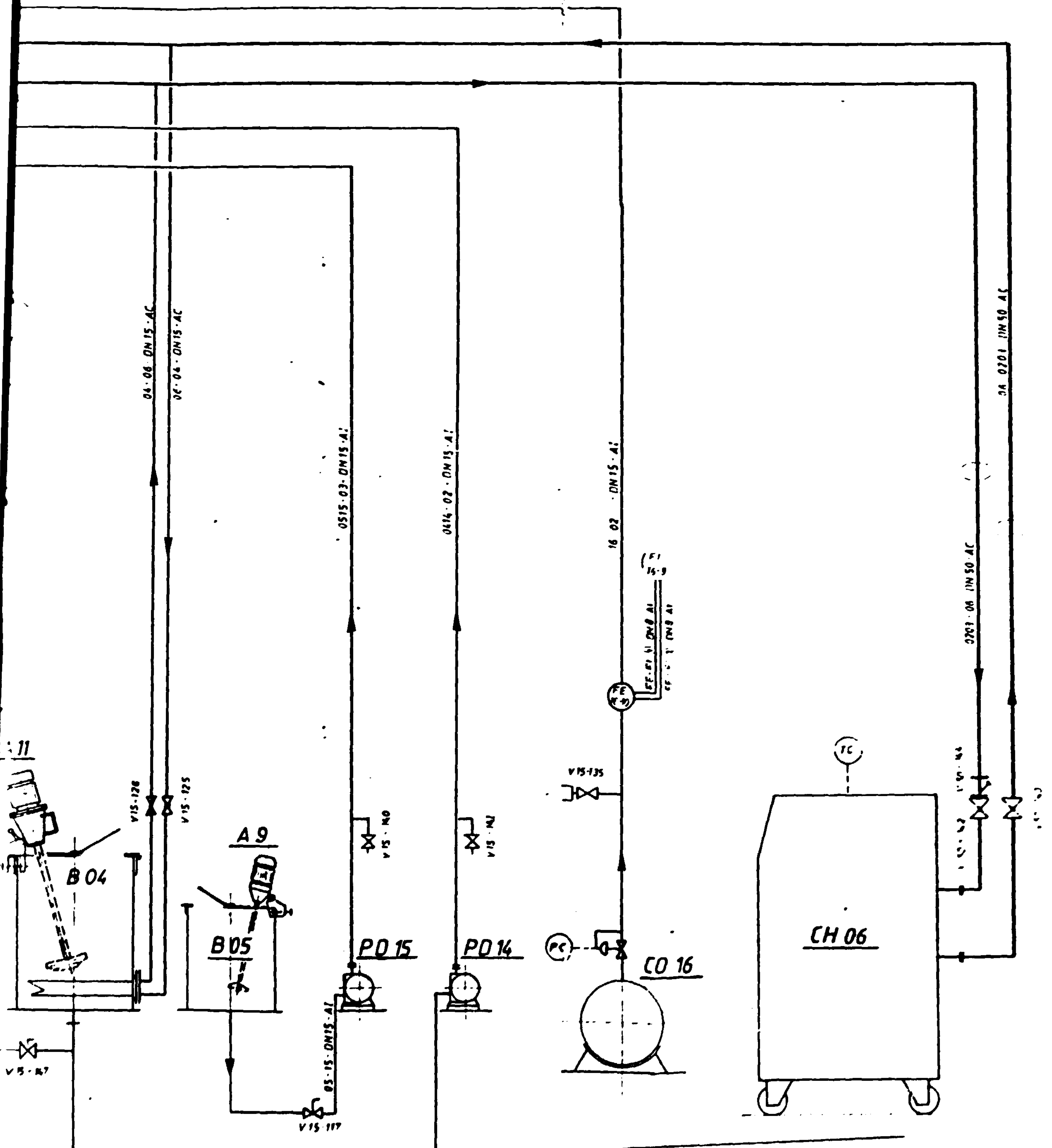
06 - 16 DN 15 - AI

SECTION 2


04 · 06 · DN 15 · AC
06 · 04 · DN 15 · AC
0515 · 03 · DN 15 · AI
0616 · 02 · DN 15 · AI
16 02 · DN 15 · AI
FI 16·9
FE
0201 · 08 · DN 50 · AC
0A 0201 · DN 50 · AC
V15 · 126
V15 · 125
V15 · 135
V15 · 140
V15 · 141
V15 · 117
V15 · 118
V15 · 147
A 9
B 04
B 05
PD 15
PD 14
PC
CO 16
TC
CH 06
05 · 15 · DN 15 · AI
06 · 16 · DN 15 · AI

SECTION 3