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CONTRACT n° 90/146

PROJECT N° US/GLO/85/151

DEVELOPMENT

OF THE APPLICATIONS

OF LIQUID NATURAL RUBBER

FINAL REPORT

INSTITUT DE RECHERCHES SUR LE CAOUTCHOUC

IRCA-CIRAD (CIRAD-CP)

**Département du Centre de Coopération Internationale en
Recherche Agronomique pour le Développement**

12 Square Pétrarque - 75166 Paris - France

CONTRACT N° 90/146

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**DEVELOPMENT OF THE APPLICATIONS
OF LIQUID NATURAL RUBBER**

FINAL REPORT

**REPUBLIQUE DE COTE D'IVOIRE
MINISTERE DE LA RECHERCHE SCIENTIFIQUE**

**INSTITUT DES FORETS (I D E F O R)
DEPARTEMENT PLANTES A LATEX (D P L)**

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I. SUMMARY AND CONCLUSIONS

I.1. Introduction

Contract US/GLO/81/059 "Production and Development of Liquid Natural Rubber" led to a pilot unit being set up and developed in Côte d'Ivoire to produce 200 kg of liquid natural rubber per run. The following contract, US/GLO/85/151, made it possible to perfect the pilot unit and develop new rubber grades derived from natural rubber.

An international meeting, attended by representatives of IRRDB member Institutes and top level experts, was held in Abidjan, Côte d'Ivoire, from 4th to 8th December 1989. The meeting was held to assess the results obtained by CIRAD-IRCA, mandated by IRRDB to implement this project financed by UNIDO from special funds made available by the Federal Republic of Germany. During the round table to sum up the meeting, the experts proposed asking UNIDO to extend the contract with a view to fulfilling the following four objectives :

- provision of bulk supplies of liquid rubbers and blends at latex stage, as well as modified liquid rubber, for continued industrial evaluation,
- change in the method of waste disposal using a cheaper process involving clarification and natural evaporation,
- installation of improved air injection and mixing facilities in the reaction chamber of the pilot plant,
- development of a cationic method of producing epoxidized liquid natural rubber (positive pH) for improved economy.

The work carried out in the 1990 transition year, then in 1991 and 1992, represents an extension to contract US/GLO/85/151, to enable fulfillment of the above four objectives.

I.2. Production of liquid rubber, modified or not

The main problem encountered in LNR production at the pilot stage, was its lack of storage stability. Fundamental work, carried out in a university context, showed that this phenomenon was the result of secondary reactions, whose effects could be cancelled out by maintaining a maximum degree of medium oxygenation. Trials in the laboratory, then in the pilot unit, led to the development of a method for monitoring the medium's oxidation-reduction potential. Introduction of the reducing agent over a period of several hours and installation on the pilot unit of an innovative device ensuring better oxygenation of the medium led to the production of liquid rubber that was stable during storage, whilst resulting in substantial savings in the reducing agent, phenylhydrazine. It is now possible to link the molecular weight of the end-product to the initial amount of phenylhydrazine introduced.

The process for the production of high molecular weight, low molecular weight rubber blends, has been developed on an industrial scale in an estate factory near the pilot unit. These blends offer interesting processing characteristics, measured in the laboratory and tested in industry.

I.3. Effluent treatment

A simple and cheap effluent treatment method was applied to the coagulation serum and water from the first washing process rejected during liquid rubber production: decantation followed by filtration through natural fibres eliminated the main solids in suspension, thereby leading to a clear serum; this

serum was then naturally evaporated on a concreted area, thereby avoiding any contamination. The residues were incinerated.

I.4. Pilot unit modification

The work carried out during the first phase of contract US/GLO/85/151 showed that it was possible to improve the quality of the air-latex mixture, so as to favour maximum activity of the oxygen in the air: testing of a turbine specially adapted for the preparation of fine gas dispersal in a liquid was successful, provided that the air injection device was modified. The air has to be injected beneath the said turbine through a device comprising two perforated tubes in the form of a cross. The bottom of the reactor was therefore modified and a manhole added, for easier cleaning of this air injector if required.

Other improvements were made to the pilot unit: installation of an anti-foaming agent atomizer, to provide better control of foam development at the start of the reaction, a solvent injection system upstream from the thin layer dryer to facilitate drying.

I.5. Epoxidized liquid rubber production

The laboratory tests carried out on site, then transposed to the pilot stage, enabled a reduction in the reaction time for liquid rubber latex epoxidation from 48 to 24 hours, with no notable changes in the final properties of the product. In the laboratory, direct depolymerization of hevea latex in an acid medium (pH of around 2.5) did not lead to such low molecular weights as those obtained with the basic pH of the conventional process. Epoxidation after depolymerization remains possible, but as the products obtained have a higher molecular weight, it is more difficult to recover them in their dry state, so transposition to the pilot stage is difficult.

Nevertheless, this study made it possible to select surfactants that make field latex inversion easier (switch from a negative pH to a very acid positive pH without coagulation) so as to obtain a positive latex. It was thus hoped to make substantial savings in the epoxidized liquid rubber production process.

I.6. Development

The Bulk Viscosity Modifier concept was developed for application at the preparation stage for rubber compounds filled loaded with carbon black by the team of a specialist in rheology working in the industry. This work has been covered in a publication and in a paper at an international conference. Contacts have been made with tyre or rubber industrialists seeking to improve the conditions for processing of their rubber, with a view to applying this Bulk Viscosity Modification concept. A technical note on IRPRENE has been produced and widely distributed. It indicates the main results obtained during the different liquid natural rubber (modified or not) development contracts. Technical data sheets are available on specific subjects.

I.7. Conclusion

The targets set for this contract extension phase have been reached: substantial quantities (8.7 tonnes) of storage-stable liquid rubber, modified or not, were produced in the pilot unit and transported to France for distribution to industry, in Europe, for assessment. The high molecular weight rubber liquid rubber blends were judged technically very interesting, since they were easier to process and gave better properties in blends. Certain industrial assessments are still under way.

New developments can be expected for epoxidized liquid rubber as a polymer plasticizer in certain synthetic elastomers, as a silica coupling agent and finally as compatibilizing agents between polymers.

It is also a very interesting raw material for grafting active molecules that can be used in fields as varied as photoreticulable varnishes, the compatibilizing agents already mentioned, delayed-action active molecule bearing polymers of interest to the phytosanitary products industry, and hevea production stimulators.

Contacts are currently being made with universities and the research centres of industrialists in the profession and certain trials are under way.

As a processing additive, liquid natural rubber is of definite interest. Epoxidized liquid natural rubber is a product that is bound to find applications in much more varied fields, some of which still remain to be explored and would justify further support from UNIDO.

II. LIQUID RUBBER AND EPOXIDIZED LIQUID RUBBER PRODUCTION

II.1. Improvement of depolymerisation reaction (LNR)

II.1.1. General

LNR is produced in latex phase through the combined action of phenylhydrazine and atmospheric oxygen. The epoxydation of phenylhydrazine gives a phenyl radical which, through addition or transfert reactions, initiates the formation of hydro and cycloperoxydes. These peroxydes lead by chain breakage to low molecular weight macromolecules ($M_v = 6000$ to 20000 , depending on the quantity of reagent used). The structure of the resulting oligomer is identical to the starting cis 1-4 polyisoprene and the chain ends are mainly carbonyl fonctions.

Fundamental work has been carried out for some years at the Université du Maine in Le Mans, to try and acquire better understanding of the mechanisms involved in natural polyisoprene depolymerization in the presence of oxygen and phenylhydrazine. This work has shown that latex is the site of two simultaneous reactions during depolymerization :

- the main reaction, i.e. phenylhydrazine oxidation, which leads to the formation of a phenyl radical acting directly upon the mechanisms that give rise to low molecular weight macromolecules through chain breakage ;
- a secondary parasite reaction which is the reaction of the phenylhydrazine with the carbonyl functions either existing naturally on the polyisoprene chains or resulting from the depolymerization reaction : combination of the phenylhydrazine with the carbonyl groups from phenylhydrazones, which are liable to oxidation and capable of forming free radicals responsible for condensation between chains leading to the increase in viscosity often seen during storage, and additional parasite consumption of phenylhydrazine.

The main reaction therefore needs to be encouraged by improving air dispersal in the medium to increase the oxygen content in the latex and by blocking the carbonyl functions with hydroxylamine sulphate (NHS).

A control method was still required for guaranteeing the excess oxygen that favours the main depolymerization reaction : this can be checked through continuous measurement of the "redox potential (RP)".

II.1.2. Definition of the redox potential

Natural rubber depolymerization results from an oxidation-reduction reaction. Oxidants can fix electrons (e). Reducers can release electrons. The relation defining the oxidant-reducer pair is as follows :



This is therefore the definition of an oxidant-reduced pair.

During the reaction, the concentrations of oxidants (air) or reducers (phenylhydrazine) vary.

When a non-corrodible conducting wire, e.g. platinum wire, is immersed in latex, it eventually assumes a balanced potential, through the continuous exchange of electrons with the solution. The corresponding formula is :

$$E = E_0 + \frac{RT}{nF} \log \frac{(OX)}{(Red)}$$

where E_0 is a typical constant of the oxidant-reducer system in question ; it is called normal potential,

R is the ideal gases constant,

T is the absolute temperature,

n is the number of electrons brought into play,

F is the Faraday number,

(Ox) and (Red) are the oxidant and reducer activities

E_0 is the oxidant-reducer potential considered, also called PR.

This measurement was made in the laboratory, then at pilot level in latex, using a portable WTW pH 91 multimeter with a TACUSSEL C8 type reference electrode and a Pt2 type platinum electrode. A +215 mV redox buffer solution was used for instrument calibration.

II.1.3. Application in the Laboratory

Laboratory tests were carried out to check latex oxygenation conditions and to check the effect of the time taken for phenylhydrazine addition on reaction quality, the final molecular weight obtained and its performance during storage. The operating conditions and results are shown in table 2.1. on the following page.

The graphs in figure 2.1. and 2.2. give an example of laboratory tests L9033 and L9022, the difference in redox potential depending on time, and the consequences for the product's final viscosimetric mass :

- L9033. After bubbling air through the medium for an hour to oxygenate it, phenylhydrazine is added drop by drop over 6 hours. The minimum redox potential (-250mV) then quickly increases to a positive value. The viscosimetric mass reached is around 8000.

- L9022. After bubbling air through the medium for half an hour to oxygenate it, phenylhydrazine is added as before drop by drop over 6 hours. The redox potential increases from minimum (-310 mV), then remains virtually stable at -290 mV. Unlike the previous case, no increase is seen. The viscosimetric mass reached is around 25,000.

The difference in process between these two operations stems from diffusion quality for the air introduced into the medium during the depolymerization reaction.

In the first case, there is 0.75 l/min for a stirring speed of 350 rpm ; in the other, it is 0.75 l/min for a stirring speed of 200 rpm.

Figures 2.1. and 2.2. shows redox potential values at the end of the reaction depending on the viscosimetric molecular weight obtained : a redox potential of almost zero or slightly higher gives a low molecular weight. All the phenylhydrazine has therefore been consumed to obtain an effective depolymerization reaction. Such results are only obtained if medium oxygenation conditions are satisfactory.

These laboratory tests led to changes in the usual operating conditions :

- pre-oxygenation of the medium through air injection,
- slow phenylhydrazine addition for 6 to 12 hours,
- air injection in sufficient quantity and stirring so as to obtain a rapid rise in redox potential once all the phenylhydrazine has been added.

LNR PRODUCTIONS AT LABORATORY SCALE IN 1990

	L9010	L9011	L9013	L9014	L9015	L9016	L9017	L9018	L9019	L9020	L9022	L9023	L9024	L9025	L9026	L9027	L9028	L9029	L9032	L9033
DATE	24/7	31/7	6/8	8/8	11/8	14/8	18/8	20/8	21/8	22/8	27/8	28/8	29/8	1/9	3/9	4/9	5/9	6/9	18/9	22/9
LATEX (I)			GT1	GT1	SEEDUNG	SEEDUNG	GT1	GT1	GT1	GT1	SEEDUNG	SEEDUNG	SEEDUNG	SEEDUNG	SEEDUNG	SEEDUNG	SEEDUNG	SEEDUNG	SEEDUNG	SEEDUNG
QUANTITY(I) [DRC = 30 %]	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
STABILISATION	Neckal	Neckal	Neckal	Neckal	Neckal	Neckal	Neckal	Neckal	Neckal	Neckal	Neckal	Neckal	Neckal	Neckal	Neckal	Neckal	Neckal	Neckal	Neckal	Neckal
SHA (%)	0	0	0	0	0	1	1	0	0	0	1	1	1	1	1	1	1	1	1	1
PHENYLHYDRAZINE (%)	8.64	8.64	8.64	8.64	8.64	8.64	8.64	8.64	8.64	8.64	8.64	8.64	8.64	8.64	8.64	8.64	8.64	8.64	8.64	8.64
INTRODUCTION TIME (h)	10	10	0.5	0.5	10	10	0.5	0.5	5	0.5	6	6	6	12	12	0.5	0.5	0.5	6	6
STIRRING VELOCITY (tr/mn)	450	200	450	450	450	450	450	450	350	350	200	225	250	350	250	350	250	250	350	350
AIR FLOW-RATE (l/mn)	0.75	0.75	0.75	0.75	2.5	1.25	1.25	1.25	0.75	0.75	0.75	0.75	0.75	0.75	1.25	0.75	1.25	0.75	1.25	0.75
AIR FLOW-RATE (l/l latex)	0.38	0.38	0.38	0.38	1.25	0.63	0.63	0.63	0.38	0.38	0.38	0.38	0.38	0.38	0.63	0.38	0.63	0.38	0.63	0.38
INITIAL REDOX POTENTIAL (mV)					-16		-113	-7	19	1	-138	-139	-121	-46	-85.0	-107	-57	-90	-46	-50
REDOX POTENTIAL AFTER PHENYL (mV)					-321	-230	-248	-308	-305	-383	-305	-295	-296	-240	-266.0	-291	-311	-297	-261	-256
FINAL REDOX POTENTIAL (mV)					-274	-204	49	-1	-66	-246	-293	-266	-259	0	-250	-41	-255	-255	27	91
Mv INITIAL	9,000	36,000	15,000	16,500	11,000	9,800	9,000	9,800	9,600	10,600	26,000	17,000	16,500	8,900	12,000	8,000	13,000	13,000	9,200	8,000
VB 25 INITIAL	126,000		270,000	507,000	182,000	112,000	94,000	130,000	119,000	141,000		422,000	447,000	92,000	238,000	88,000	303,000	347,000	116,000	120,000
VB 25 after 1 month	201,000		401,000	460,000	210,000	145,000	105,000	160,000	135,000	201,000		500,000	587,000	128,000	250,000	106,000	355,000	425,000	159,000	134,000
VB 25 after 2 months	194,000		366,000	400,000	223,000	135,000	129,000	175,000	148,000	197,000		530,000	600,000	137,000	270,000	140,000	377,000	500,000	152,000	137,000
VB 25 after 3 months	185,000		336,000	365,000	217,000		132,000	155,000												
EVOLUTION AFTER 1 MONTH (%)	59.5		48.5	(9.3)	15.4	29.5	11.7	23.1	13.4	42.6		18.5	31.3	39.1	5.0	20.5	17.2	21.8	37.1	11.7
EVOLUTION AFTER 2 MONTHS (%)	54.0		35.6	(21.1)	22.5	20.5	37.2	34.6	24.4	39.7		25.6	34.2	48.9	13.4	59.1	24.4	43.3	31.0	14.2
EVOLUTION AFTER 3 MONTHS (%)	46.8		24.4	(28.0)	19.2		40.4	19.2												

Table 2.1.

KINETICS OF DEPOLYMERIZATION

WITH N.H.S.

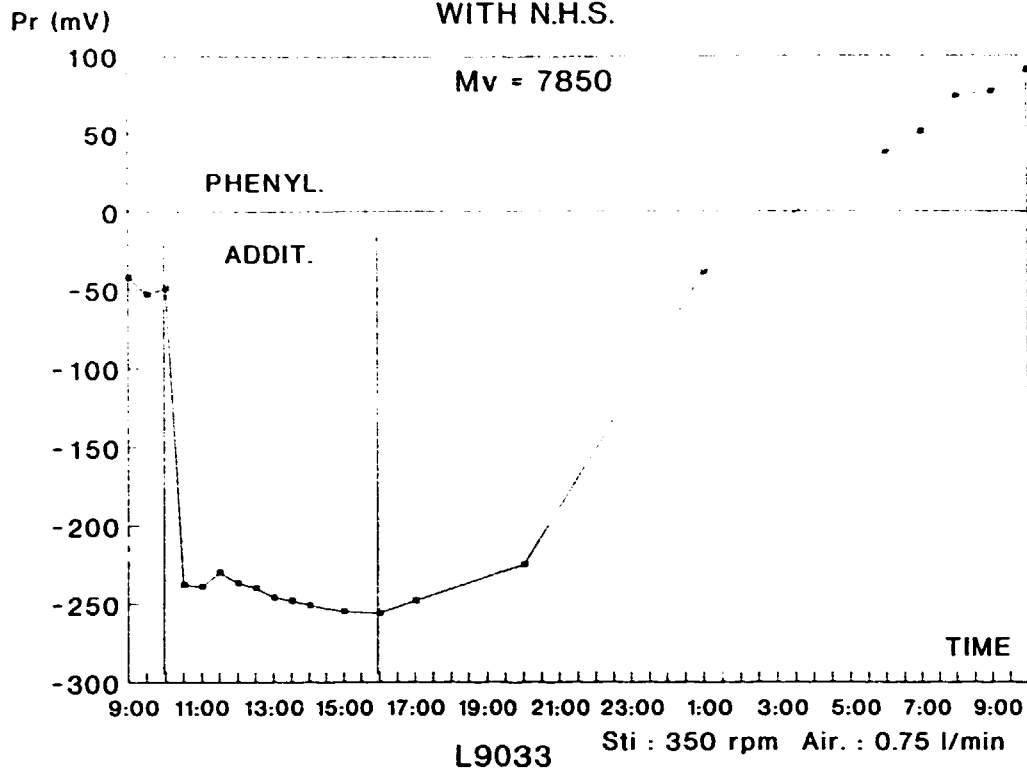


Figure 2.1

KINETICS OF DEPOLYMERIZATION

WITH N.H.S.

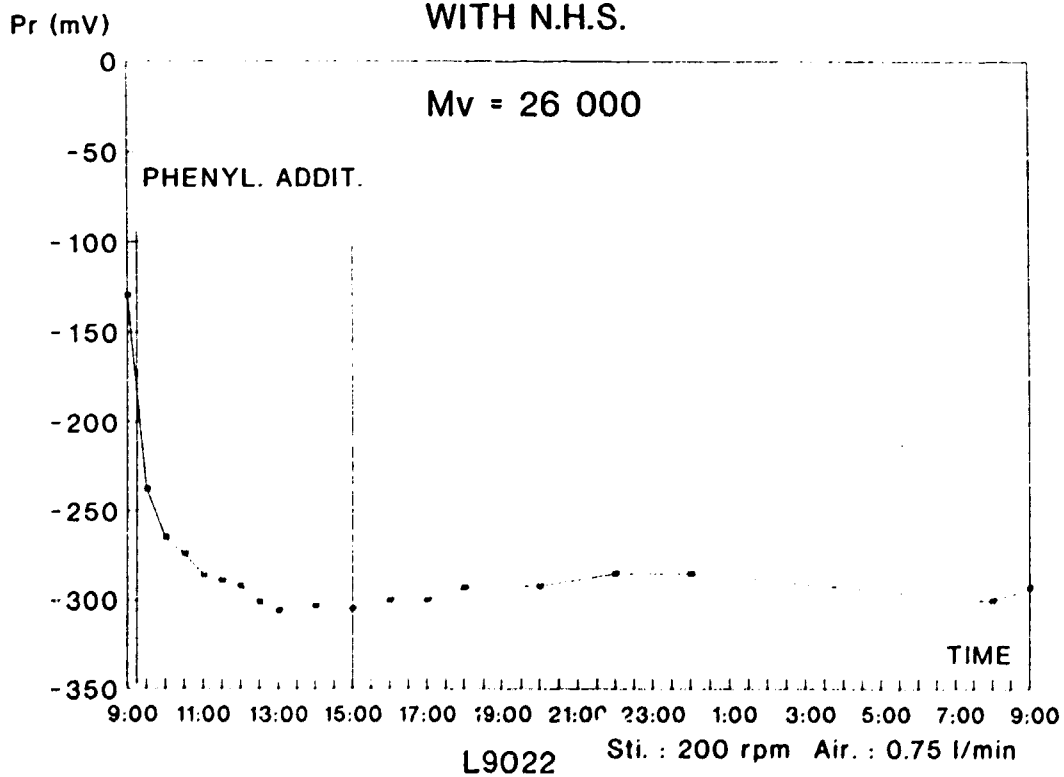


Figure 2.2

Additional trials described below were carried out in the laboratory, varying the phenylhydrazine content between the standard value PH 10 and 0.5 times the standard value $0.5 \times \text{PH } 10$. The operating conditions, some of which are shown in table 2.2., were as follows:

- Neckal Bx surfactant
- PH 10
- 24 hour latex stabilization
- 3 hour preoxygenation
- stirring speed: 350 rpm
- medium temperature : 65°C

Figure 2.3. illustrates the results in table 2.2., showing the relationship existing between the phenylhydrazine rate and the viscosimetric molecular weight of the end-product. The asymptotic curve shows that beyond $0.8 \text{ PH } 10$, a viscosimetric molecular weight of 5,000 (considered the limit) is obtained.

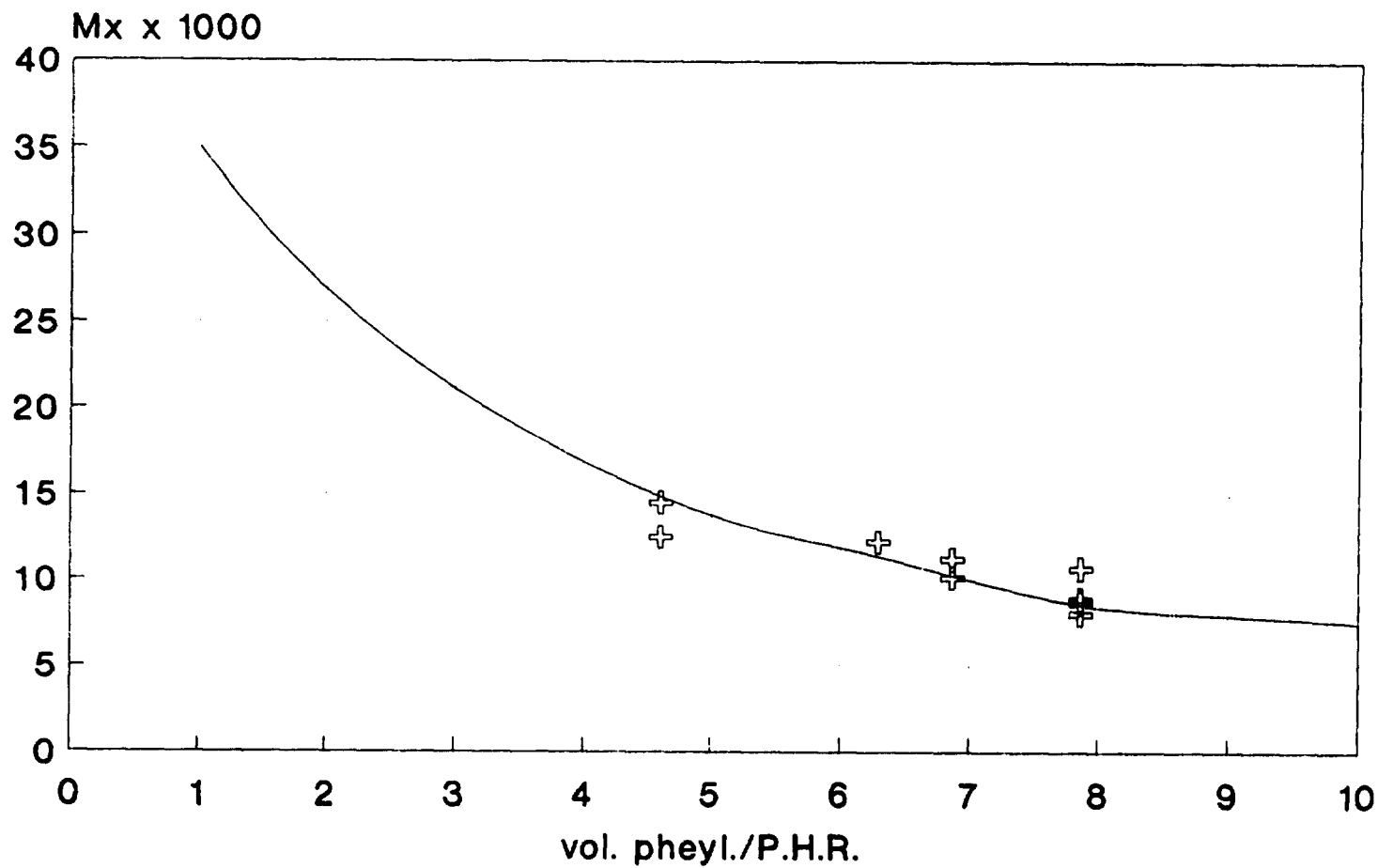
In table 2.2., examination of the values $M_v(x)$ days and $V_b(x)$ days confirms that this procedure results in liquid rubbers whose viscosimetric molecular weights and Brookfield viscosities remain stable during storage.

	L9107	L9108	L9109	L9110	L9111	L9112
Date	12/7/91	17/7/91	17/7/92	19/7/91	19/7/91	23/7/91
Latex	GT1	GT1	GT1	GT1	GT1	GT1
Amount of latex (g) DRC = 30%	896	896	896	896	896	896
Neckal Bx phr	1	1	1	1	1	1
SHA phr	1	1	1	1	1	1
Phénylhydrazine (%)	PHIO	PHIO	0,75 x PHIO	0,75 x PHIO	0,5 x PHIO	0,5 x PHIO
Introduction time (h)	7	7	7	7	7	7
Air flow (l/min)	0,75	0,75	0,75	0,75	0,75	0,75
Agitation speed (rpm)	350	350	350	350	350	350
Initial Mv -	6200	5300	9820	9250	18250	14430
Initial Vb	71000	74000	281000	239000	945000	445000
Mv (days)	7260 (464)	7550 (459)	13500 (460)	12630 (458)	23690 (461)	19150 (457)
Vb (days)	150600 (461)	147000 (456)	417500 (456)	384000 (454)	>2M(454)	1040000 (449)

Table 2.2. RELATION BETWEEN PHENYLHYDRAZINE RATION AND
FINAL MOLECULAR WEIGHT

VISCOSIMETRIC MOLECULAR WEIGHT/ PHENYLHYDRAZINE AMOUNT

7 h. introduction



LABORATORY SCALE

Figure 2.3.

II.1.4. Confirmation in the Pilot Unit

In order to confirm the laboratory results, 17 trials were conducted in the pilot unit in 1990, 1991 and 1992. The operating conditions are given in tables 2.3. (1990), 2.4. (1991), 2.5 (1992): latex origin (seedling or clone), surfactant type, mass of the original dry rubber, presence or not of hydroxylamine sulphate, phenylhydrazine content and introduction time, turbine rotation speed, compressor operating time (in relation to the amount of air introduced), quantity of anti-foaming agents introduced, pressure. The original viscosimetric molecular weight and viscosity characteristics and those after one or two months are indicated for each trial. Figure 2.4. shows the changes in redox potential over time, the phenylhydrazine being introduced at time zero in the figure, over a period of 6.5 hours. The end of the depolymerization kinetics is shown on the left-hand side of figure 2.4. The changes in redox potential: drop and low plateau during the first eight hours of the reaction, then a rise when the depolymerization kinetics become asymptotic, show the advantages of working with slow phenylhydrazine introduction (plateau) and continuing medium oxygenation so as to remove the risk of secondary reaction development mentioned in section II.1.1.

The relationship between the final viscosimetric molecular weight and the amount of phenylhydrazine is shown in figure 2.5, confirming that beyond 8 phr of phenylhydrazine, it is not possible to obtain a lower viscosimetric molecular weight.

Finally, the storage stability of liquid rubber was monitored for three production batches from the pilot unit, P9206, P9207 and P9208. Figure 2.6 illustrates the changes: after two months, there were virtually no further changes in viscosity. During the first two months following production, viscosity resumption, expressed in centipoises measured with a Brookfield viscometer, doubled.

	P9001	P9002	P9003	P9004	P9005	P9006	P9007
Operation date	26/2/90	14/5/90	8/10/90	15/10/90	22/10/90	5/11/92	26/11/92
Latex	Seed.	Seed.	Seed.	PB86/s.	PB86/s.	PB86/s.	PB86/s.
CC mass in kg	204,7	247	227.5	206	150	152	153
Stabilization	Neckal	Neckal	Neckal	Neckal	Neckal	Neckal	Elfapur
NHS (%)	1	1	1	1	1	0	0
Phenylhydrazine (%)	8.64	8.64	8.64	8.64	8.64	8.65	8.64
Phenylhydrazine addition (hrs)	-	-	6	7	6,5	6	6
Stirring speed (rpm)	175	122	175	175	217	217	217
Compressor operation (hrs)	142	8.5	17.2	15.9	14.6	11.9	11.8
10% anti-floaming agent (ml)	700	140	1350	550	150	100	200
Pressure (atm)	0	0	0	1	1	1	1
Initial Mv	13800	13400	12400	10400	6300	-	-
Initial Vb	-	-	226500	221700	125000	259000	-
Vb after 1month	-	-	321000	293000	266000	289000	-
Vb after 3months	-	-	607500	487000	286000	358000	-

Table 2.3. RESULTS OF LNR PILOT EXPERIMENTS IN 1990

	P 9105	P 9106	P 9107	P 9108
Operation date	23/09/91	11/10/91	13/12/91	20/12/91
Latex	Seed/GT1	GT1	Seed/GT1	GT1
CC mass in kg	180	183.2	181.5	152.4
Stabilization	Neckal	Neckal	Neckal	Neckal
NHS (%)	1	1	1	1
Phenylhydrazine (%)	5.05	5.05	8.64	5.05
Phenylhydrazine addition (hrs)	7	7	8	4
Stirring speed (rpm)	217	217	217	217
Compressor operation (hrs)	4.39	4.25	3.75	3.71
10 % anti-floaming agent (ml)	425	575	325	275
Pressure (atm)	1	1	1	1
Initial Mv	18940	11130	8 800	14500
Initial Vb	800 000	430 000	292 000	515 000
Vb after 1 month	-	-	345 600	650 000
Vb after 3 months	-	-	396 000	758 000

Table 2.4. RESULTS OF LNR PILOT EXPERIMENTS IN 1991.

	P9209	P9212	P9214	P9215	P9219	P9220
Operation date	5/6/92	18/7/92	6/8/92	13/8/92	23/10/92	30/10/92
Latex	GT1	GT1	GT1	GT1	GT1	GT1
CC mass in kg	167	167	150	152	159	162
Stabilization	Neckal	Neckal	Neckal	Neckal	Neckal	Neckal
NHS (%)	1	1	1	1	1	1
Phenylhydrazine (%)	7.54	8.64	6.91	6.91	6.91	8.64
Phenylhydrazine addition (hrs)	7	7	7	7	7	7
Stirring speed (rpm)	217	217	217	217	175	175
Compressor operation (hrs)	3.74	4.20	3.84	3.86	3.62	3.77
10 % anti-floaming agent (ml)	225	125	250	300	475	275
Pressure (atm)	1	1	1	1	1	1
Initial Mv	10140	8860	12180	12200	20110	10230
Initial Vb	207000	176000	238000	230000	965000	230000
Vb after 1 month	306000	191000	323000	266000	-	-
Vb after 3 months	355000	252000	336000	-	-	-

Table 2.5. RESULTS OF LNK PILOT EXPERIMENTS IN 1992

KINETICS OF DEPOLYMERIZATION P9005

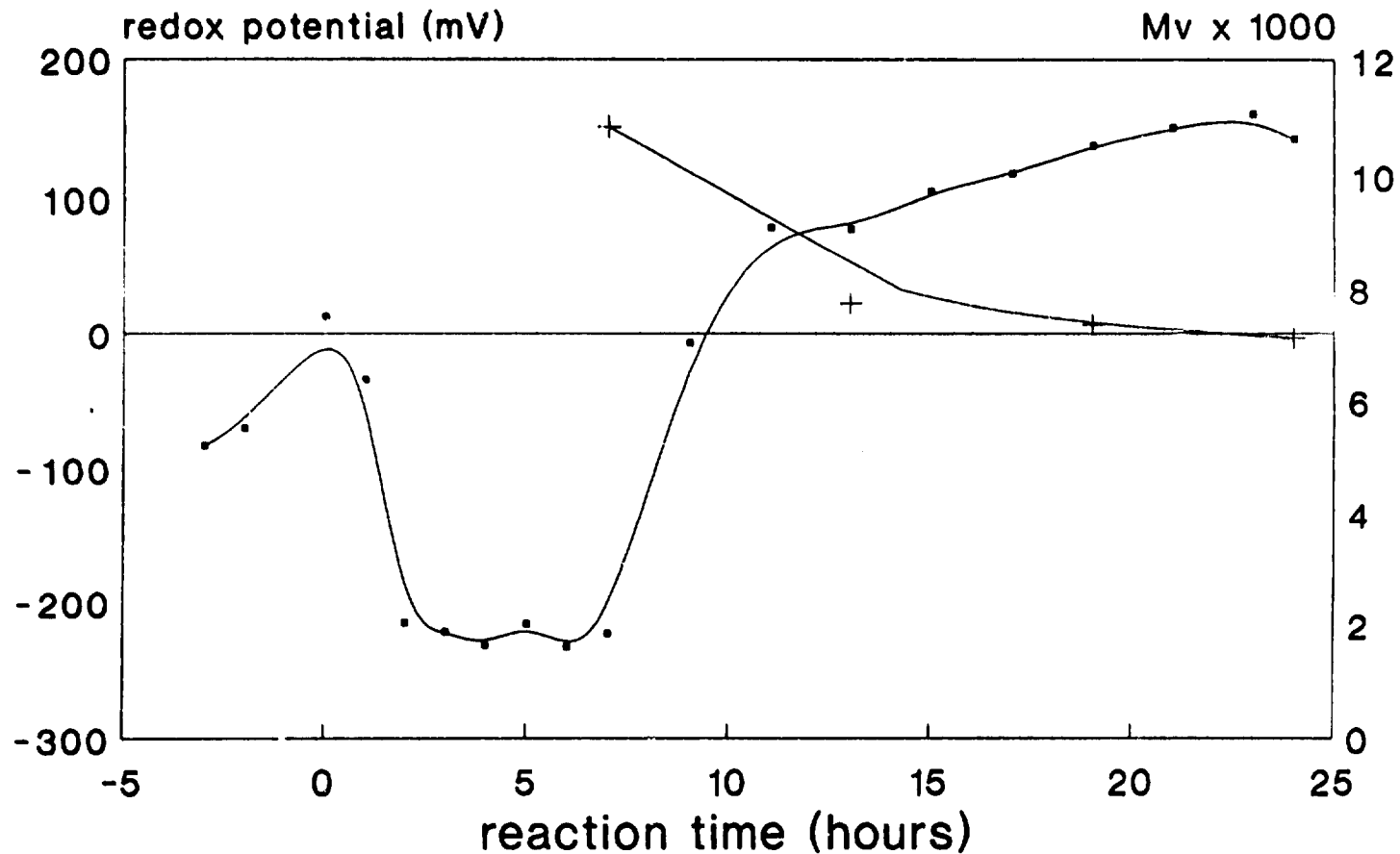
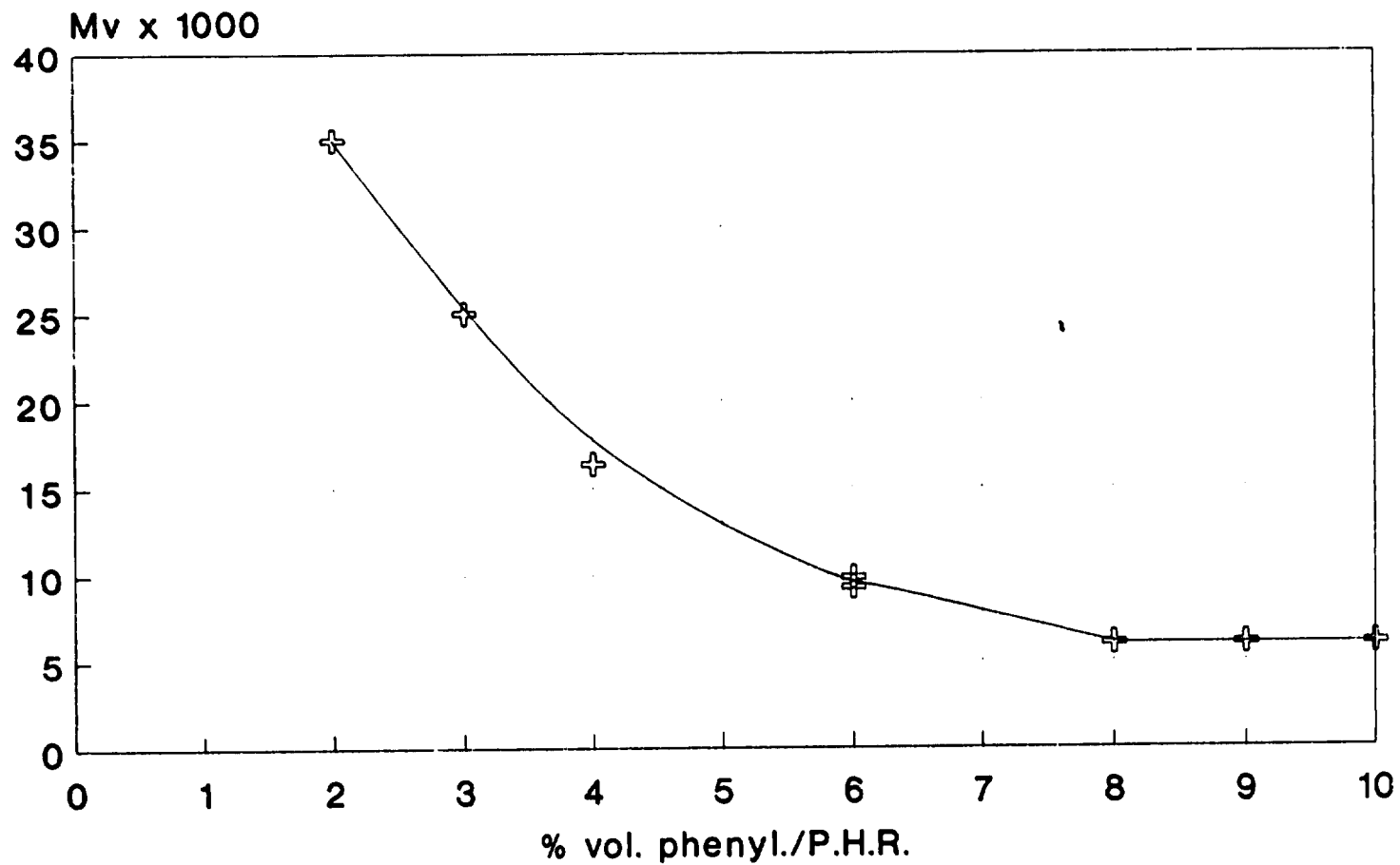


Figure 2.4.

VISCOSIMETRIC MOLECULAR WEIGHT/ PHENYLHYDRAZINE AMOUNT

7 h. introduction



PILOT SCALE

Figure 2.5

LNR STABILITY PILOT SCALE

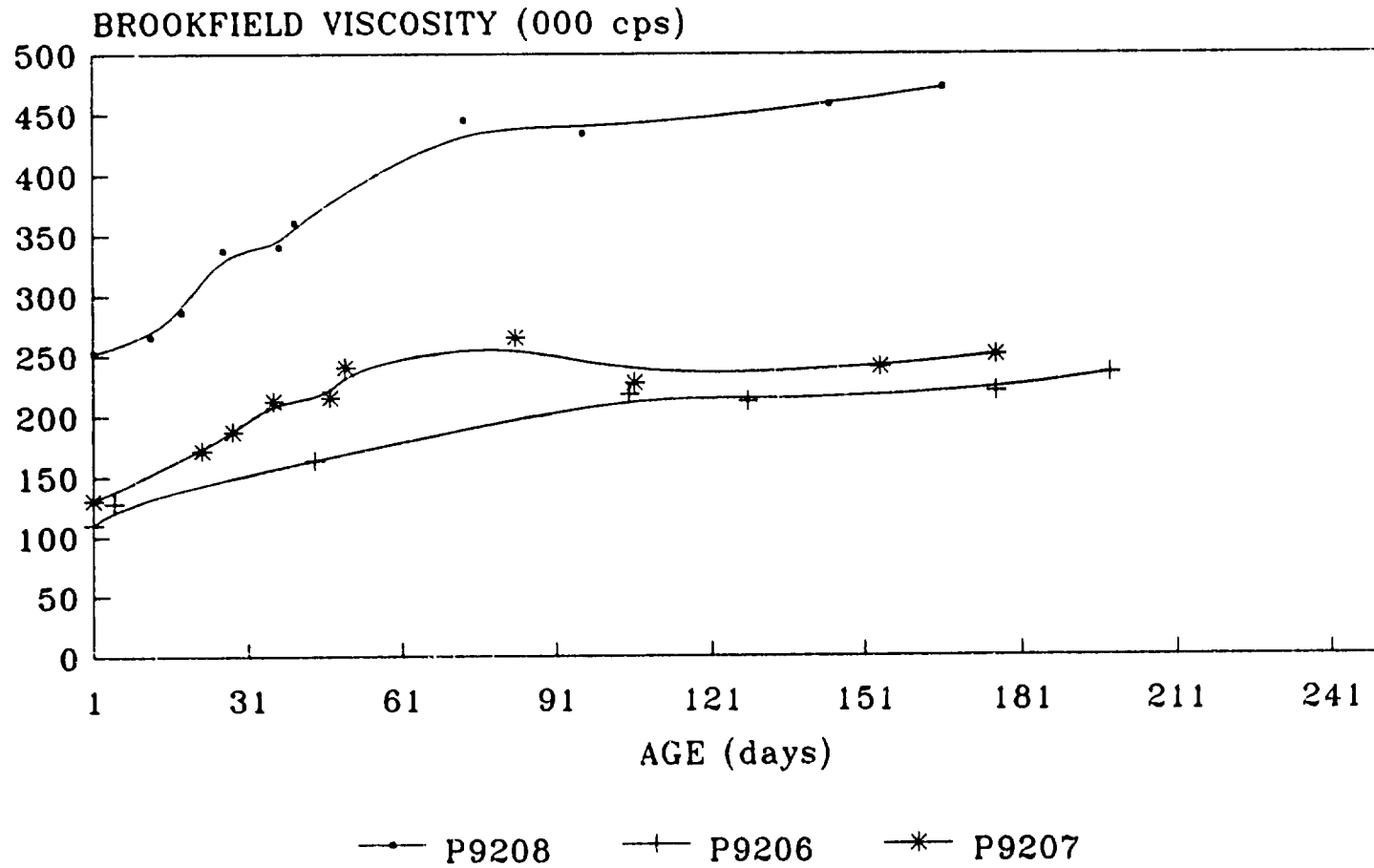


Figure 2.6

II.2. Epoxydation

II.2.1. *Reminder*

Under the last UNIDO contracts, epoxidation of depolymerized natural rubber latex was transposed to the pilot stage.

The general process for preparing epoxidized liquid natural rubber called ELNR involves 4 main stages:

- 1st stage

NR latex stabilization: the stabilizer surfactant has to be non-ionic or cationic since epoxidation is carried out in an acid medium.

- 2nd stage

Depolymerization as per the conventional phenylhydrazine + air procedure; it is important to remember that whatever the nature of the stabilizer, the depolymerization level obtained is more or less the same.

- 3rd stage

Epoxidation reaction: the epoxidation agent is therefore the peracid formed "in situ" and the quantity will depend on the epoxidation rate aimed for.

- 4th stage

ELNR recovery, which is carried out in 4 phases:

1st phase:

Neutralization to pH 7-7.75, to prevent later secondary reactions.

2nd phase:

Coagulation: if the latex is cationic surfactant, neutralization with soda causes coagulation; if the surfactant is non-ionic, coagulation is obtained either by adding methanol (laboratory method), or by heating to a temperature higher than the stability limit (method applicable to the pilot unit scale).

3rd phase:

Coagulum washing.

4th phase:

Drying

N.B. A stage 4a consists in keeping the epoxidized liquid rubber latex as it is, with gentle stirring, ready for mixing after neutralization to pH 7 with field latex to obtain a high molecular weight/low molecular weight rubber blend, as indicated in section III.

Two channels were explored during this phase of the project with a view to improving reaction yields and reducing costs:

- reduction of the hydrogen peroxide action time
- "cationic" acid pH depolymerization

II.2.2. Reduction of the epoxidation time

Some preliminary work carried out by IRAP (Institut de Recherches Appliquées sur les Polymères) showed that it was possible to reduce the duration of the actual epoxidation reaction by 50%, i.e. after the start of hydrogen peroxide introduction, with a secondary aim of limiting cycle openings?

Three laboratory trials were conducted under the following conditions:

- 300 g of rubber from clone GT1 with an initial DRC of 40%
- stabilization for 24 hrs in the presence of soda (1.7 cm³ of solution at 27%), hydroxylamine (1 phr) and Elfapur N150 (3 phr)
- depolymerization: stirring at 350 rpm; air flow: 750 cm³/min; preoxygenation: 3hrs, 24 ml of phenylhydrazine, 24 h polymerization reaction, DRC = 30%, temperature 65°C.
- epoxidation:

- . formic acid $\frac{\text{HCOOH moles}}{\text{LNR moles}} = 0.15$
- . hydrogen peroxide $\frac{\text{H}_2\text{O}_2 \text{ moles}}{\text{LNR moles}} = 0.5$ instead of the theoretical 0.37
- . other parameters : stirring speed 75 rpm, temperature 60°C, latex pH 2.5, DRC 20%

- rubber recovery

- . neutralization by 41.5 cm³ of soda solution at 27%, i.e. 5.6 phr, final pH 7.3
- . thermocoagulation in 2½ hours at 90°C
- . drying in a vacuum in 2½ hrs
- . residual hydrogen peroxide before neutralization 2.3 0.2 phr

- mean properties of the end product

- . viscosimetric molecular weight of the LNR, 5,600
- . theoretical epoxidation rate 25%, actual rate, 25.3 0.4%
- . olefin rate 66.4 0.8%
- . cycle opening rate: 8.3 1.2%

It is therefore possible, subject to slight over-consumption of hydrogen peroxide, to reduce the epoxidation rate from 48 to 24 hrs. The operating procedure was transferred to the pilot unit.

II.2.3. Depolymerization in a cationic medium

Liquid rubber depolymerization is carried out in a basic medium, which means that the latex has to be inverted - switched from a basic pH to an acid pH - so that it can then be epoxidized. It therefore appears to be more logical to perform a depolymerization reaction in an acid pH, to avoid inversion. Preliminary trials conducted in France on centrifuged latex enabled the appropriate surfactant to be

chosen (Elfapur N150). Three trials were conducted in the Ivory Coast on field latex under the following conditions:

- Field latex, DRC 40%, stabilized with ammonia, equivalent to 300 g of dry rubber
- Stabilization with 3 phr of Elfapur N150 with DRC reduced to 20% for 24 hrs, final pH 8.8.
- Depolymerization:
 - . pH brought to 2.7 by acidification with 35.8 g of formic acid at 85%
 - . preoxygenation, 3 hours stirred at 350 rpm
 - . standard phenylhydrazine rate
 - . air flow: 750 cm³/min
 - . reaction time: 24 hrs
- Rubber recovery by latex neutralization with soda to pH 7.14, thermocoagulation at 90°C for 3 hrs and drying.
- Characteristics of the final product: $M_v = 17,500 \quad 1,000$ with a Brookfield viscosity approaching 600,000.

With field latex, depolymerization in an acid medium (cationic) gives a product with too high a molecular weight and viscosity for the epoxidized liquid rubber to be recovered under satisfactory conditions. Only the production of epoxidized liquid rubber latex remains possible.

II.2.4. *Production in the pilot unit*

In 1991 and 1992, production in the pilot unit had two objectives: experimental work and the provision of samples for industry within the 10% and 25% modification rate range. As seen in section 6, production underwent "bag-in-box" packaging, i.e. a polyethylene bag containing 5 kg net of product, in a plywood box, and was then shipped to France for distribution to industrialists. The operating conditions and the properties of the products obtained are given in tables 2.6, 2.7 and 2.8.

	P 9101	P 9102	P 9103	P 9104
Operation date	04/02/91	19/04/91	10/05/91	17/06/91
Latex	GT1	GT1	Seed/GT1	PB86/GT1
CC mass in kg	156	150	150	150
Stabilization	Elfapur	Elfapur	Elfapur	Elfapur
NHS (%)	1	1	1	1
Phenylhydrazine (%)	8.64	8.64	8.64	8.64
Phenylhydrazine addition (hrs)	7	7	7	7
Stirring speed (rpm)	217	217	217	217
Compressor operation (hrs)	10.7	11.1	11.8	11.9
10 % anti-foaming agent (ml)	50	75	75	75
Pressure (atm)	1	1	1	1
Initial Mv	7230	9000	10400	7500
Expected epoxydation rate (%)	25	25	25	25
Obtained epoxydation rate (%)	19	15.8	27.2	26.3
Oleifin rate (%)	72	80	63.5	64.6
Opening rate (%)	9	4.2	9.3	12.1

Table 2.6. RESULTS OF ELNR PILOT EXPERIMENTS IN 1991.

	P 9203	P 9204	P9210	P9211
Operation date	07/02/92	29/02/92	23/06/92	07/07/92
Latex	GT1	GT1	GT1	GT1
CC mass in kg	163	172	169	167
Stabilization	Elfapur	Elfapur	Elfapur	Elfapur
NHS (%)	1	1	1	1
Phenylhydrazine (%)	8.64	8.64	8.64	8.64
Phenylhydrazine addition (hrs)	7	7	7	7
Stirring speed (rpm)	217	217	217	217
Compressor operation (hrs)	3.85	3.66	4.14	4.02
10 % anti-foaming agent (ml)	275	300	250	300
Pressure (atm)	1	1	1	1
Initial Mv	6000	6800	7460	7560
Expected epoxydation rate (%)	25	10	25	25
Obtained epoxydation rate (%)	23.5	13	24.8	25.3
Oleifin rate (%)	62.1	79.4	67	62.6
Opening rate (%)	14.4	7.6	8.2	12.1

Table 2.7. RESULTS OF ELNR PILOT EXPERIMENTS IN 1992.

	P 9213	P 9216	P9217	P9218
Operation date	29/07/92	25/08/92	08/09/92	22/09/92
Latex	GT1	GT1	GT1	GT1
CC mass in kg	163	160	160	162
Stabilization	Elfapur	Elfapur	Elfapur	Elfapur
NHS (%)	1	1	1	1
Phenylhydrazine (%)	8.64	8.64	8.64	8.64
Phenylhydrazine addition (hrs)	7	7	7	7
Stirring speed (rpm)	217	217	217	217
Compressor operation (hrs)	4.13	4.03	3.77	4.21
10 % anti-foaming agent (ml)	350	525	325	500
Pressure (atm)	1	1	1	1
Initial Mv	8280	10890	8840	10430
Expected epoxydation rate (%)	25	25	40	25
Obtained epoxydation rate (%)	23	18.2	27.6	21
Oleifin rate (%)	68	72.5	57.1	72.5
Opening rate (%)	9	9.3	15.3	6.5

Table 2.8. RESULTS OF ELNR PILOT EXPERIMENTS IN 1992.

III. PREPARATION OF LNR/NR AND ELNR/NR BLENDS

III.1. Introduction

A certain number of preliminary trials were conducted to adapt the preparation and processing procedure to the industrial conditions at the Anguédédou factory which processes the natural rubber of the surrounding estate and IDEFOR DPL (ex IRCA) plantations. Only blends at 5% non-modified latex and 5 or 10% modified latex can be produced under the working conditions in this factory. The latexes produced in the pilot unit are Mv: 8,000 or 15,000 (LNR/NR blend) and Mv: 8,000, epoxidation rate 25% (ELNR/NR blend).

III.2. Latex preparation in the pilot unit

- modified or not, these latexes should be stirred continually to avoid creaming, which is detrimental to final homogeneity,
- in the case of epoxidized latexes, prior neutralization is necessary with soda, final pH 7,
- latex DRC determination.

III.3. Blending of the two latexes in the factory

In order to make optimum use of bulking tank blending capacity, it takes at least 3,200 litres of field latex with a known DRC. The volume of depolymerized rubber latex, modified or not, is calculated according to the DRC values and the blending rate sought. Depolymerized rubber latex (modified or not) was introduced without taking any particular precautions, by syphoning out of the drums from the pilot unit.

It is necessary to keep stirring the latex mixture for 15 min, to ensure good homogenization.

Coagulation and maturing were carried out according to the usual industrial procedures: volume of acetic acid determined from the acidification curve, maturing in a coagulation trough for 16 hours.

III.4. Processing and drying

After maturing for 16 hours, the coagulum was pressed in a crusher; the band obtained was cut up and the coagulum creped according to the usual cup lump line procedure, for better washing (elimination of residual chemicals), careful homogenization of the end-product, and mechanical elimination of the maximum amount of serum.

The crepes were then crumbed in a crusher-hammermill on the secondary grade line, then dried for 4 hours at around 100°C in a KGSB type industrial drier. The dry crumb was then weighed and pressed into 35 kg bales.

III.5. Technical characteristics of these rubbers

The table III.1. below gives the characteristics of the following blends:

Type	Molecular weight of liquid rubber	Degree of modification	% LNR/ELNR compared to total
Y0021 (control)	0	0	0
80 NR 95 Y0023	8,000	0	5
150 NR 90	15,000	0	10
80 E 25 NR 90	8,000	25	10

Examination of the raw rubber qualities in comparison with the control containing no depolymerized rubber, reveals:

- 1) The expected plasticizing effect, due to the incorporation of the liquid polymer, modified or not: drop in Po and Mooney viscosity (MV) values.
- 2) Stabilization of rubber viscosity during storage: ASHT test lower than 6 Wallace plasticity points.
- 3) Stronger rubber coloration: Lovibond greater than 6 in all cases.
- 4) In the case of high molecular weight/epoxidized liquid rubber blends only, an abnormally high dirt content, no doubt due to the presence of sodium formate from inversion of the depolymerized rubber before epoxidation (reduction in pH from 10 to 2.5 through massive addition of formic acid), then its neutralization; more rigorous washing in the factory should eliminate this product.
- 5) Lower PRI values for the blends, though remaining within the specification limits for the better grades.

In a pure ACS gum blend accelerated by MBT, examination (see table III.2.) of the vulcanization characteristics measured with a rheometer reveals :

- a) The "scorching" effect of epoxidized liquid rubber: value of T5 lower than 40% for blends Y0037 and Y0038.
- b) Except for blend Y0036, the minimal effect of adding depolymerized rubber on the vulcanization condition measured by MHR - M_L , whereas an examination of the hardness (HARD) and 100% modulus values (M 100) revealed no loss in property for these two characteristics in vulcanized blends.

To sum up, these results clearly show the merits of high molecular weight/liquid rubber blends as natural polymers with improved processing characteristics.

Anguédédou Blending Trials

	Control (Y0021)	Blend 80 NR 95 (Y0023)	Blend 150 NR 90 (Y0036)	Blend 80 E 25 NR 90 (Y0037)	Blend 80 E 25 NR 90 (Y0038)
DIRT	0,021	0,023	0,021	0,34	0,24
ASH	0,22	0,23	0,13	0,18	0,17
VM	0,31	0,35	0,22	0,11	0,10
Nit	0,37	0,41	0,40	0,38	0,37
Po	41	29	23	22	23
PRI	88	83	70	68	65
Moon.	72	56	47	42	42
Col	6	12	15	13	11
ASHT	11	2	3	1	1
ACSI compound					
Moon.	47,5	37,5	42,5	30,5	30
M100	0,593	0,626	0,520	0,579	0,604
HARD	30	30	30	31	31,5
T5	9'04"	8'09"	8'13"	5,34	5,05
MHR	4,746	4,520	3,955	4,24	4,35
ML	1,525	1,186	1,130	1,07	1,07
t'c(90)	11,95	8,80	8,85	10,4	9,5
ts1	1,65	1,40	1,55	1,2	1,1

Table III.2.

IV. PILOT UNIT IMPROVEMENT

The diagram of the final version of the pilot unit is given on the last page of this report; four improvements were made under this contract.

IV.1. Epoxidized liquid rubber production using the cationic method

The pilot unit was fitted with equipment for rubber depolymerization in an acid medium with a pH of around 2.5, in compliance with the procedure indicated under § II.2.1:

- addition of a 150-l stainless steel tank, equipped with a variable speed stirrer for stabilized latex preparation using non-ionic surfactants, and a diaphragm pump for latex transfer to the reactor, R01. This pump is now also used for the direct transfer of field latex stored in 200-l drums used for routine production not requiring positive latex preparation.

The process can be summed up as follows :

- non-preserved latex from the fields,
- addition of this latex to a solution of Noramium NCS0 or Elfapur 150 and formic acid (due to the risk of coagulation, this will be done in a completely open 150-litre stainless steel tank),
- transfer to R02,
- depolymerization,
- phenylhydrazine/air, T = 65°C : duration : 24 hrs,
- residual phenylhydrazine titration,
- transfer to R03,
- epoxidation with H₂O₂,
- soda coagulation,
- washing,
- drying.

IV.2. Improvement of depolymerization reaction conditions

In order to further improve the contact between the air and the latex, reactor R01 was modified to take a Ruchton turbine, designed to ensure much finer dispersion of air in the latex; a cross-shaped device has been installed below this turbine to optimize air injection under the turbine. There is a manhole in the bottom of the reactor for effective cleaning of the cross-shaped device if necessary.

IV.3. Anti-foaming system

A large quantity of foam is always produced at the beginning of the depolymerization reaction, which has to be destroyed by adding the appropriate anti-foaming agent. In order to prevent the troublesome development of such foam, reactor R01 has been fitted with an atomizer designed to deliver a fine mist of silicon-based anti-foaming agent, thereby reducing the amount of foam to a strict minimum.

IV.4. Thin-layer drier cleaning device

After each liquid rubber production operation, with modified rubber or not, the thin-layer drier has to be cleaned, without removing the central rotor. This operation can be carried out simply by washing the rotor and inside walls with the appropriate solvent, toluene or "Pergasol". This is why a funnel with a solvent reserve has been installed upstream of the "Mag" coagulum injection pump.

V. EFFLUENT TREATMENT

The effluent treatment method adopted is as follows (see schematic diagram 5.1.)

Fresh serum - pilot unit

Decantation

Filtration through cocorut fibre

Evaporation

Incineration of remaining sludges

A 100 m² leak-proof floor has been laid for rapid evaporation of effluents from which solid particles have already been removed. In fact, decantation means that rubber particles can be recovered from the surface (density = 0.9) and the remaining impurities and flocculates are removed by filtering. The virtually particle free serum is poured onto this evaporation floor (see diagram in figure 5.2).

In order to speed up evaporation and prevent rainwater from filling this area, a light roof in black polyethylene will be placed over it.

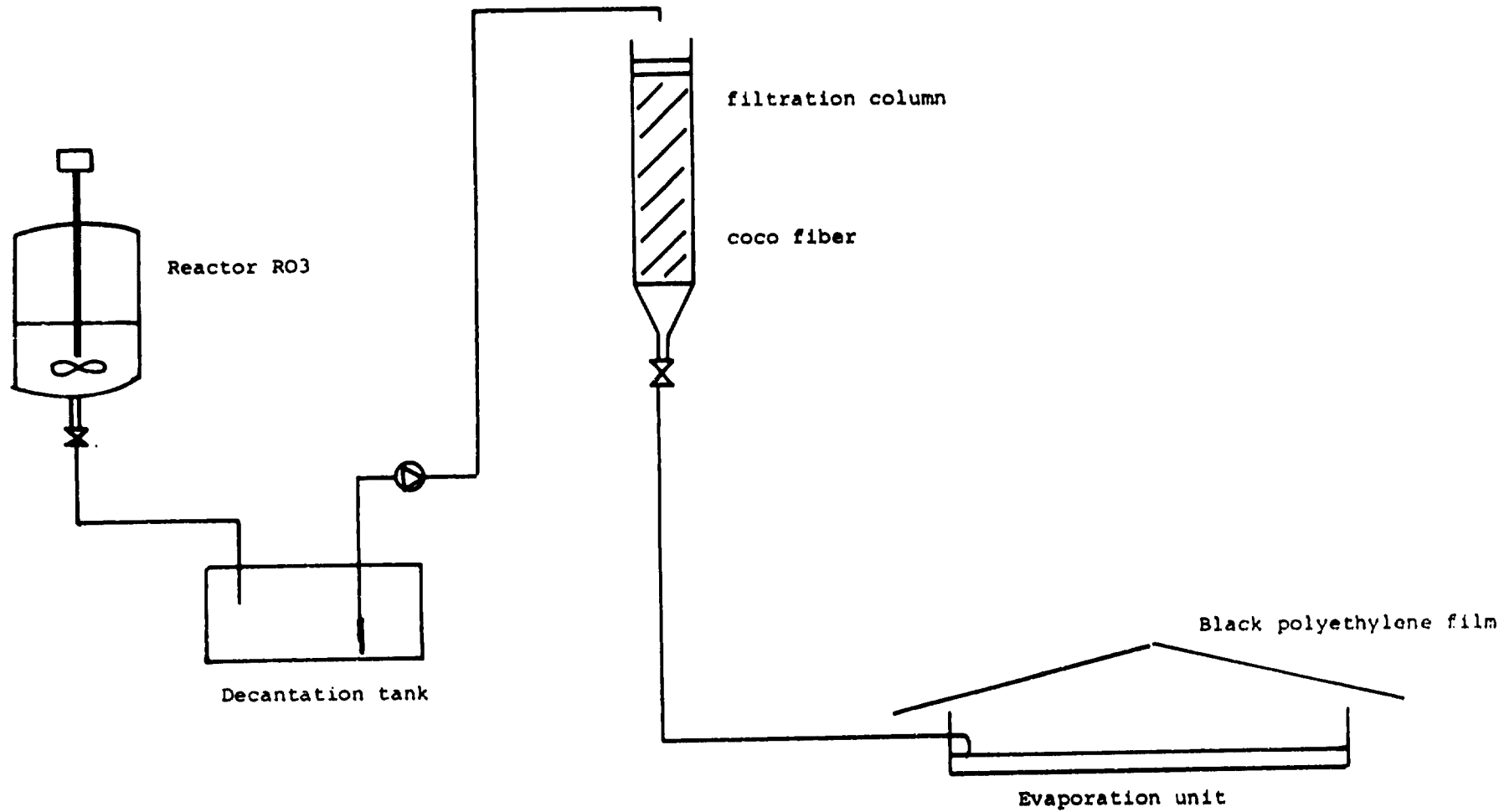
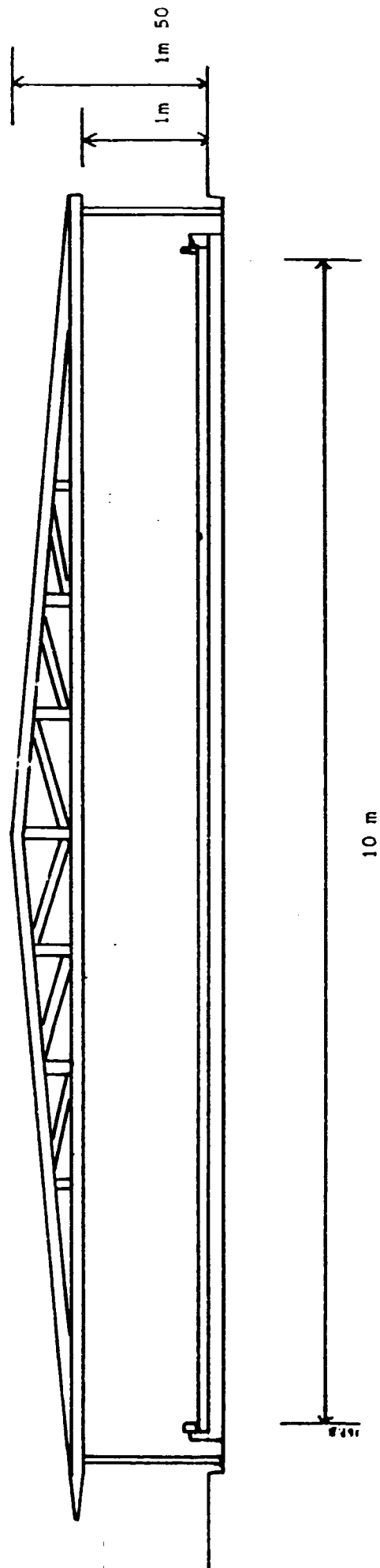


FIGURE 5.1. LAYOUT OF EFFLUENT TREATMENT UNIT

FIGURE 5.2. LAYOUT OF THE EVAPORATION FLOOR



VI. DEVELOPMENT

VI.1. Expanding the Bulk Viscosity Modifier concept

The Bulk Viscosity Modifier concept described in Abidjan during the Workshop on Liquid Natural Rubber (1, 2, 3) in 1989 was applied this time to the preparation of blends loaded with carbon black: comparison of the effect of a processing oil with a liquid rubber having a molecular weight of 8,000. The main results of the study are given below (2).

A Natural Rubber formulation was used to compare the effect of increasing level of Liquid Natural Rubber and Processing Oil on the processing properties. The formulation studied are given in Table 6.1.

Table 6.1. : Test formulation

Compound Nr :	1	2	3	4	5	6	7
SMR SCV ^(a)	100	100	100	100	100	100	100
N330 Carbon black	40	40	40	40	40	40	40
LNR ^(b)	-	4	7	10	-	-	-
Dutrex 729 oil ^(c)	-	-	-	-	4	7	10

Zinc Oxide : 5 - Stearic Acid : 2 - Sulfur : 2.5 - CBS^(d) : 0,6

^(a) premasticated to ML₍₁₊₄₎ 40-45 at 100°C - ^(b) Liquid Natural Rubber - M_n = 7800
^(c) aromatic processing oil - Shell Chemical Co
^(d) accelerator - N-cyclohexyl-2-benzothiazolesulfenamide

Mixing operations : a single pass procedure controlled with respect to energy levels, all the mixing parameters (i.e. instantaneous power, energy, ramp position, rotor speed and temperature) recorded.

The filler incorporation time is shorter with LNR, whatever the level considered. The benefit offered by the Liquid Natural Rubber is clearly understood when considering the ram position traces (Figure 6.1.). As can be seen, only 4 phr of LNR produce a significant shortening of the time to close the chamber and the optimum benefit is obtained at 7 phr. Increasing amounts of processing oil also decrease the chamber closure delay but in a lesser extent. Other mixing data confirm the advantages offered by Liquid Natural Rubber, i.e. lower dump temperature and power at dump, and shorter filler dispersion time. The specific energy figures for all the batches show that all the experiments were made in similar conditions.

The viscosity properties were assessed with a capillary rheometer at 100°C. A series of 1 mm diameter dies with various length-to-diameter ratios (i.e. 1,5 and 10) were used. The drastic difference between the LNR and the Oil is clearly seen when plotting the relative viscosity variation (in % with respect to the viscosity of the reference compounds) versus the additive level (Figure 6.2.) : the effect of the LNR is proportional to content, while the effect of the oil tends to plateau out above 5 phr.

As BVM, the Liquid Natural Rubber is acting as molecular level and therefore the viscoelastic properties of the compound are expected to be modified in a such a way that the viscous component rather than the elastic one is modified. In practical terms, both the processing oil and the LNR are expected to decrease the elastic and the viscous components, but the loss on the elastic character is expected to be lower with the bulk viscosity modifier.

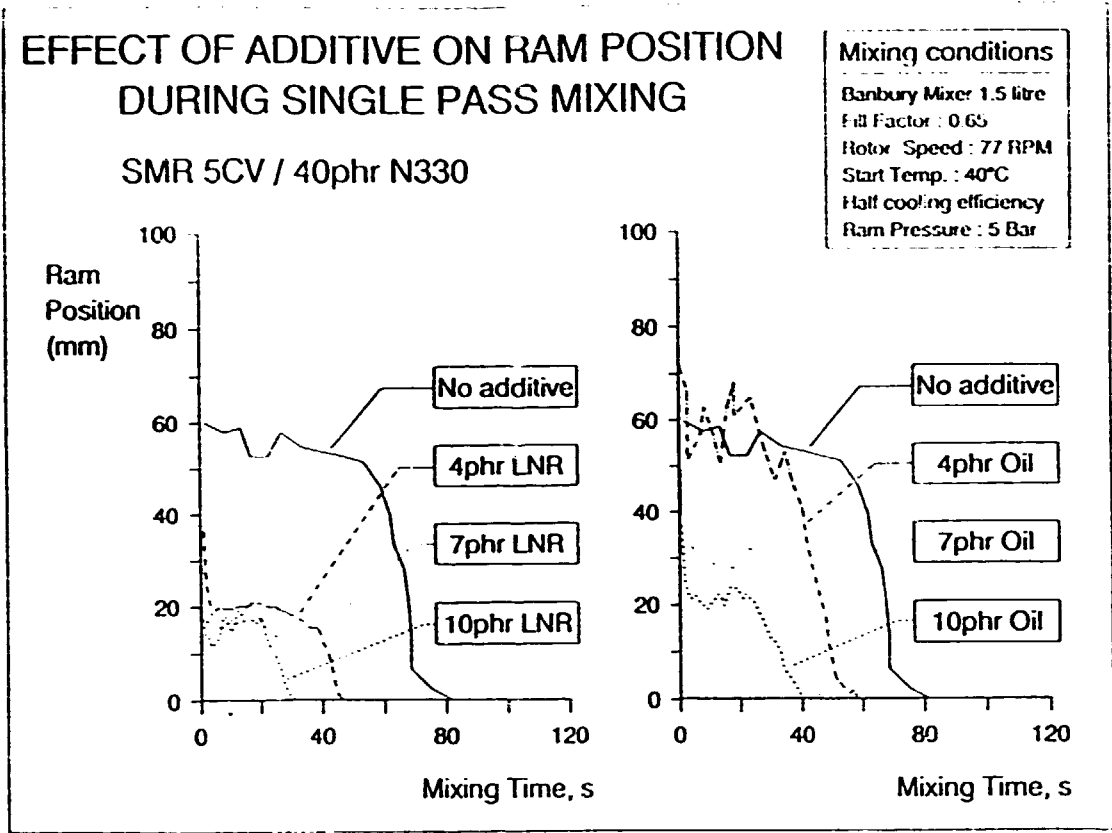


Figure 6.1

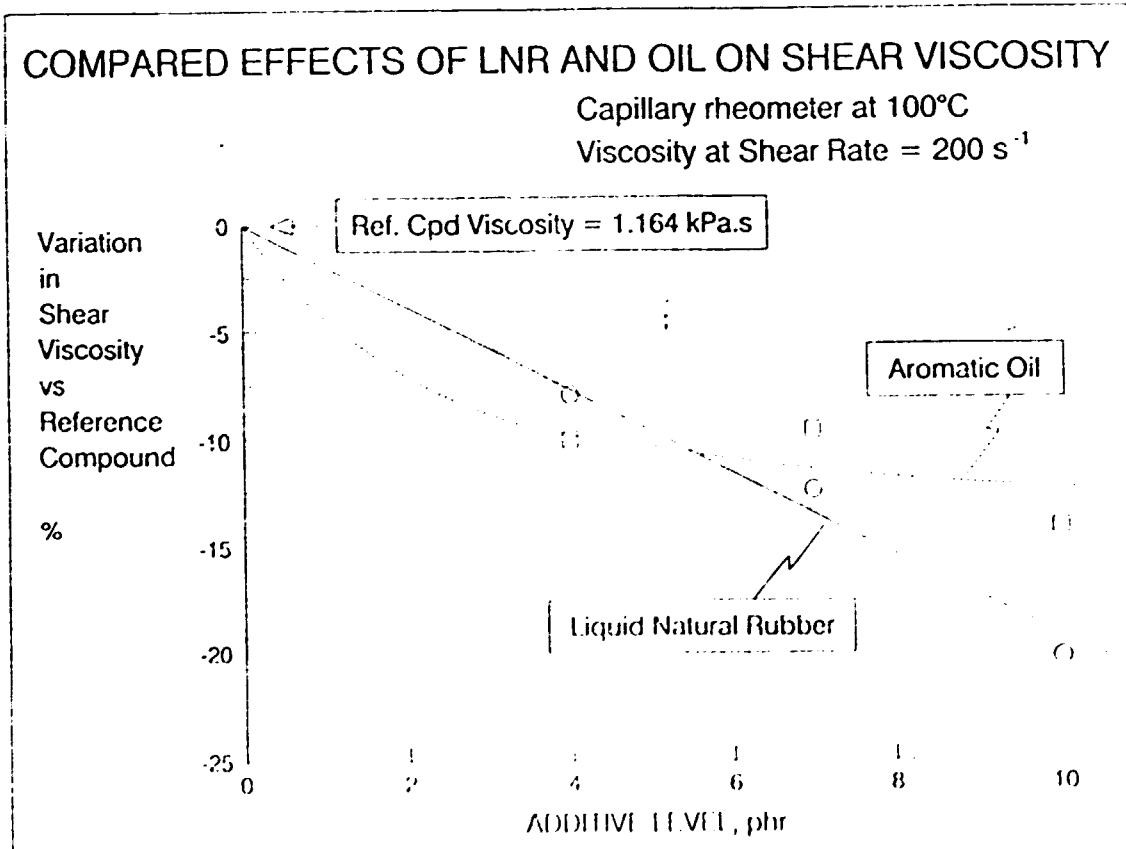


Figure 6.2

EFFECTS OF LNR AND OIL ON VISCOELASTIC PROPERTIES

Monsanto RPA 2000 at 110°C - Strain sweep test at 10.47 Rad/s frequency

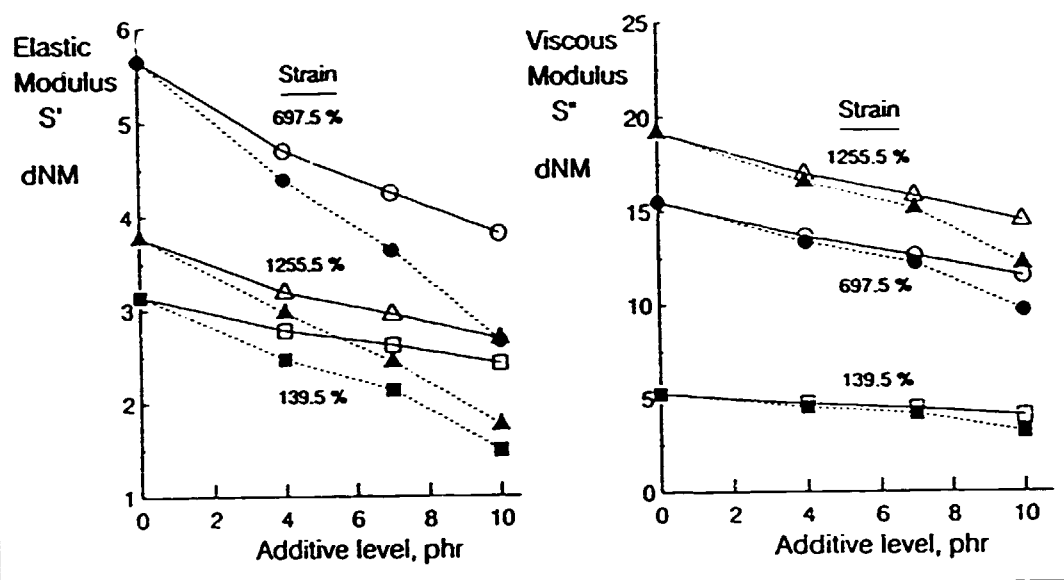
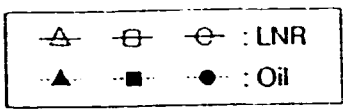


Figure 6.3

To analyse the effect of both additives on the viscoelastic properties of the rubber compounds investigated, experiments were performed with the RPA 2000, a new instrument being developed by Monsanto to provide in a single test both elastic and viscous information. When performing a strain sweep test at constant frequency, at the same temperature (Figure 6.3.) drastic losses on elasticity with the oil can be seen, as well as a slightly larger decrease on the viscous modulus.

The advantages of Bulk Viscosity Modifier result from the high compatibility of such species with elastomers and the consequent fact the flow properties are modified without drastic changes in the boundary conditions, i.e. essentially the wall slippage. There are obviously a number of molecules which could exhibit the BVM character, but Liquid Natural Rubber is an interesting one because of its unique macromolecular features and the flexibility of the depolymerization process. Further studies are obviously needed but one of the most important conclusions from this paper is the high potential of LNR in allowing the process of compounds otherwise impossible to handle. Such a demonstration can only be made in the rubber processing plant.

VI.2. Development of liquid rubbers in industry

VI.2.1. *The IRPRENE series*

Under the previous contract (4), the name IRPRENE was given to liquid natural rubbers, along with a code to identify the different products.

- LNR (Liquid Natural Rubber) : the designation is followed by figures indicating the mean viscosimetric molecular weight (Mv) in hundreds.

e.g. IRPRENE-95C for a production with an Mv of 9500

- ELNR (Epoxidized LNR) : the designation is followed by 2 groups of figures : the first indicating the mean viscosimetric molecular weight (Mv) in hundreds before epoxidation, the second indicating the epoxidation rate as a percentage.

e.g. IRPRENE-95E25

- Blend : Blend rubber is a grade 5 "off latex" rubber : the ponderal rate of basic rubber varies from 80 to 95 %. The designation is as follows : IRPRENE + 2 or 3 figures giving the Mv of the depolymerized component, followed by NR and 2 figures giving the proportion (as a %) of high mass rubber.

e.g. IRPRENE 95-NR95, blending at 5 % depolymerized rubber with a molecular weight of 9,500 (Mv).

The system is similar for blending the epoxidized product.

e.g. IRPRENE 95E25-NR95, blending at 5 % depolymerized rubber with a molecular weight of 9,500 (Mv) and a 25 % epoxidation rate.

IRPRENE

IRPRENE 95 C 6000 < Mv < 16000
 ↑ ↙
 Mv = 9 500 Castable (LNR)

IRPRENE 95 E 25
 ↗ ↑ ↖
 Mv = 9500 Epoxidized (ELNR) % double bonds modified

IRPRENE 95 NR 95
 ↗ ↖ ↖
 Mv = 9500 NR = 95 % LNR = 5 %

IRPRENE 95 E 25 NR 95
 ↗ ↑ ↑ ↖
 Mv = 9500 ELNR % double bonds modified ratio NR 95 % ELNR = 5 %

Table 6.2. lists the potential applications for different IRPRENES.

BRANCHS	USES
<p data-bbox="419 650 591 685">ADHESIVES</p> <p data-bbox="401 738 608 773">AUTOMOTIVE</p> <p data-bbox="448 919 559 954">SHOES</p> <p data-bbox="410 963 596 998">CHEMICALS</p> <p data-bbox="398 1006 608 1041">COMPOSITES</p> <p data-bbox="430 1050 576 1085">LEATHER</p> <p data-bbox="436 1094 570 1129">SEALING</p> <p data-bbox="430 1137 576 1172">CLOTHES</p> <p data-bbox="355 1225 652 1260">TECHNICAL GOODS</p> <p data-bbox="430 1312 570 1347">MEDICAL</p> <p data-bbox="445 1356 556 1391">PAINTS</p> <p data-bbox="457 1399 544 1434">TIRES</p> <p data-bbox="419 1574 588 1609">COATINGS</p> <p data-bbox="372 1618 634 1653">ADHESIVE TAPES</p>	<p data-bbox="917 663 1158 694">Softener of epoxies</p> <p data-bbox="969 707 1100 738">Hot-melts</p> <p data-bbox="899 751 1173 781">Anti vibration mounts</p> <p data-bbox="882 794 1191 825">Hoses and radiator tubes</p> <p data-bbox="888 838 1185 869">Windscreen wiper blades</p> <p data-bbox="888 882 1185 912">Seals for door and body</p> <p data-bbox="1007 926 1071 956">Soles</p> <p data-bbox="902 969 1173 1000">Material for reactions</p> <p data-bbox="984 1013 1092 1043">Softener</p> <p data-bbox="972 1057 1103 1087">Waterproof</p> <p data-bbox="914 1100 1161 1131">Jointing compounds</p> <p data-bbox="955 1144 1121 1174">Rubber bands</p> <p data-bbox="969 1188 1106 1218">Disposables</p> <p data-bbox="1007 1231 1071 1262">Belts</p> <p data-bbox="891 1275 1185 1306">Industrial rubber goods</p> <p data-bbox="949 1319 1126 1349">Hospital goods</p> <p data-bbox="908 1362 1167 1393">Primers and bonders</p> <p data-bbox="969 1406 1106 1437">Tire treads</p> <p data-bbox="928 1450 1144 1480">"Bead compound"</p> <p data-bbox="879 1493 1202 1524">Confection of trucks tires</p> <p data-bbox="931 1537 1150 1568">Economical tubes</p> <p data-bbox="905 1581 1176 1611">Ebonite/Hard coatings</p> <p data-bbox="940 1624 1141 1655">Adhesive Masses</p>

Table 6.2. Potential branches of "IRPRENE"

VI.2.2. New product packaging device

Liquid rubber packaging was revised, to adapt it to industrial requirements, particularly those of the tyre industry. Expensive and not very practical 200-l drums were replaced by 5-litre capacity bags in cardboard boxes or plywood crates adapted to the weight and volume of the product.

The system offers industrialists 5 kg units of liquid rubber that are easier to handle and can be emptied directly into the internal mixer.

Polyethylene bag specifications

- polyethylene bags with expandable sides
- VICAT 50-55 point
- 18 % EVA
- length = 520 mm
- width = 240 mm
- 110 mm concertina

A pneumatic pump has been installed for filling the bags. Its characteristics are as follows : GRACO BULLDOG type pneumatic pump, ratio 4:1, flow-rate 9 l/min at 70 cycles assembled on a double-action, double column pneumatic elevator, equipped with an air input regulator and follower plate for 200-l drums.

VI.2.3. Industrial contacts

Table 6.3. summarizes the qualities and quantities of liquid rubber, modified or not, produced in 1991 and 1992.

Table 6.3. Pilot unit production in 1991 and 1992

	Quality	Production
LNR	70 C	1,993
	120 C	400
	150 C	515
	Total	<u>2,908</u>
ELNR	70E10	172
	70E20	156
	90E15	150
	100E25	150
	70E40	160
	70E25	808
Total	<u>1,590</u>	
Blend LNR/NR	70NR95	1,660
	150NR90	1,575
	Total	<u>3,235</u>
Blend ELNR/NR	80E25NR90	560
	Total	<u>560</u>

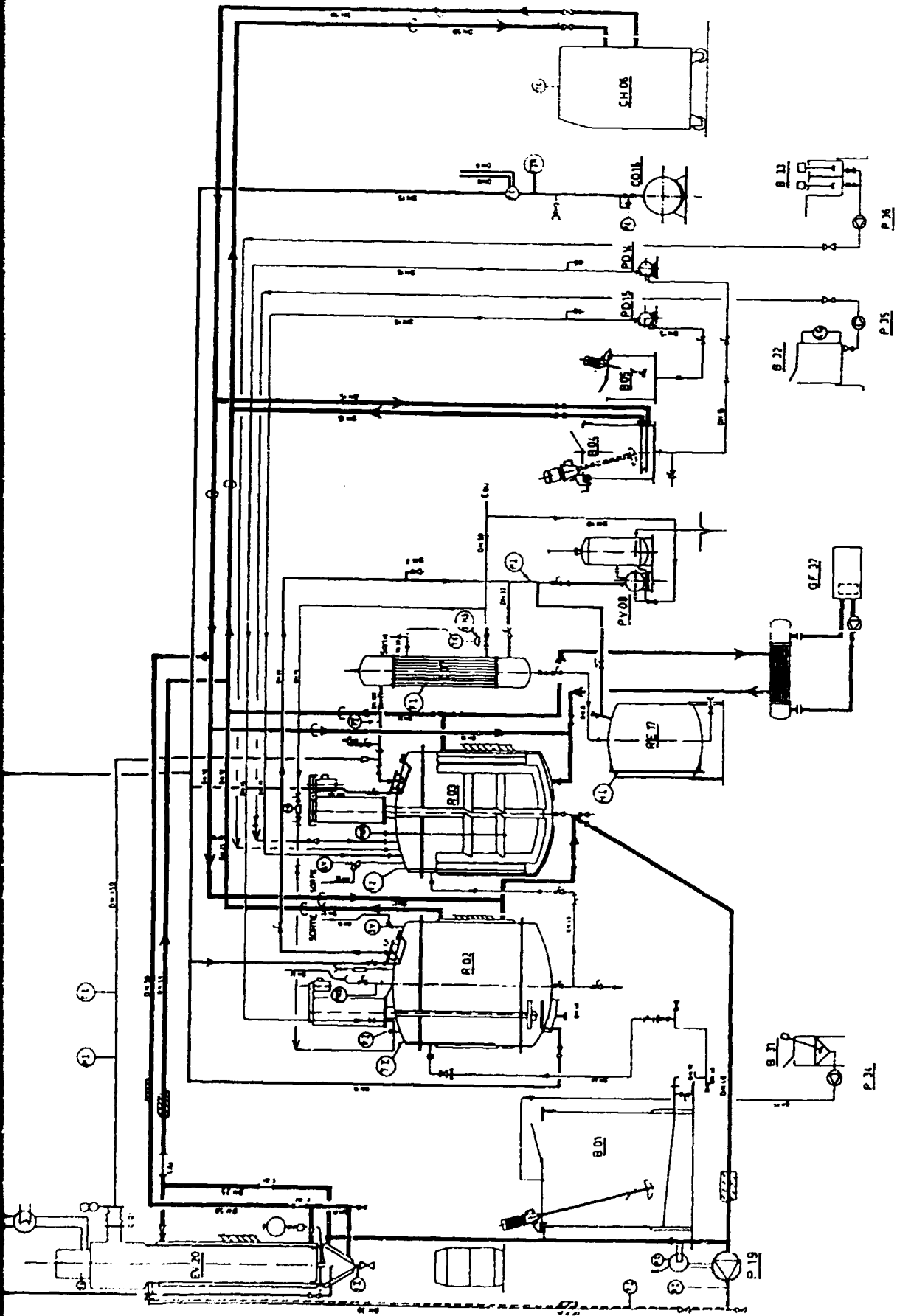
With production in the second half of 1991 and in 1992 of batches of storage-stable liquid rubber, epoxidized rubbers at reproducible rates and, finally, high and low molecular weight rubber blends, sampling was carried out with selected industrialists interested by these products. They were mainly major tyre manufacturers, technical rubber manufacturers and an industrialist producing light fillers for the tyre industry, from the following countries:

Germany	1	Italy	1
Austria	1	Great Britain	1
Belgium	1	France	5
Luxemburg	1	Thailand	1

As the use of liquid rubber led to either a gain in productivity, or an improvement in end-product quality, the results have to remain confidential. IDEFOR/DPL in the Ivory Coast (formerly IRCA/CIRAD) is kept up to date with results and is ready to produce liquid rubber, either modified or not, to satisfy demand.

At the time this report was written, three tyre manufacturers and two manufacturers of technical items were still interested in liquid rubber, essentially in blend form, which is easier to incorporate. One of the three large estate companies in the Ivory Coast is ready to cooperate with IDEFOR/DPL for the industrial manufacture of such blends.

University studies are continuing on the use of IRPRENE E epoxidized liquid rubber as a raw material for the manufacture of high added value goods: photoreticulable varnishes, delayed-reaction hevea stimulation products. A study has been launched in this respect at the training centre of the Syndicat Professionel Française du Caoutchouc for the use of IRPRENE as a plasticizer in certain synthetic elastomers and coupling agents in silica-based mixtures. Thought is currently being given with a European industrialist, universities and research centres, to the use of IRPRENE E as it is, or grafted, as an elastomer or plastics compatibilization agent, e.g. for the production of thermoplastic elastomers.



KEY

EV 20	Evaporator
B 01	Tank Latex
P 19	MAAG Pump
B 31	Soap tank
P 34	Diaphragm pump
R 02	Depolymerization reactor
R 03	Reactor
C 07	Condenser
RE 17	Sump
GF 37	Refrigeration unit
PV 08	Vacuum pump
B 04	Phenylhydrazine tank
B 05	Acid tank
PD 15	Acid pump
PD 14	Phenylhydrazine pump
CO 16	Compressor
CH 06	Boiler
B 32	Hydrogen peroxide tank
P 35	Hydrogen peroxide pump
P 36	Soda pump
B 33	Soda tank
PI	Pressure gauge (pressure indicator)
TI	Thermometer (temperature indicator)
PHS	Pressure sensor
SV	Safety valve
PHR	pHmeter
FQ	Integrating meter (flow quantifier)
FI	Flow indicator
TC	Temperature controller
THS	Thermostat
NI	Level indicator
PC	Pressure controller
LG	Level indicator window
FE	Flow measurement
FIR	Flow regulator

BIBLIOGRAPHY

1. **Liquid Natural Rubber as a Model Bulk Viscosity Modifier to control the processability of rubber compounds.** J.L. Leblanc, H. de Livonnière, G. Boccaccio. *Progress in Rubber and Plastic technology* 2, 1992, p 79.
2. **Recent development in Liquid Natural Rubber chemistry and processing aid application.** H. de Livonnière, J.C. Brosse, J. Leblanc, G. Boccaccio. *Proceeding of the Rubbercon 92*, Brighton, 1992, p. 329-334.
3. **Le caoutchouc naturel liquide et le concept de modification de viscosité en masse dans les problèmes de mise en oeuvre des caoutchoucs.** Dr J.L. Leblanc. *Compte rendu de la Conférence Internationale sur les applications du caoutchouc naturel liquide*, Abidjan, 1989, p. 45-136.
4. **Le développement et les perspectives des IRPRENE.** R.E. Brice, J.C. Touron. *Compte rendu de la Conférence Internationale sur les applications du caoutchouc naturel liquide*, Abidjan, 1989, p. 208-210.