PARTICIPAÇÃO NA CONFERÊNCIA INTERNACIONAL SOBRE BORRACHA NATURAL LÍQUIDA EM ABIDJAN, COSTA DO MARFIM

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CENTRO NACIONAL DE PESQUISA DE SERINGUEIRA E DENDÊ - CNPSD

PARTICIPAÇÃO NA CONFERÊNCIA INTERNACIONAL SOBRE BORRACHA NATURAL LÍQUIDA EM ABIDJAN, COSTA DO MARFIM

RELATÓRIO DE VIAGEM

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SUMÁRIO

1. INTRODUÇÃO

Em 1981, após um simpósio realizado na Tailândia, sobre novas formas de borracha natural, onde foram divulgados os resultados obtidos pelo IRCA e IRAP com a pesquisa de borracha líquida em escala laboratorial, um acordo foi firmado entre o IRRDB e a UNIDO (Organização das Nações Unidas para o Desenvolvimento Industrial) com a finalidade de transpor para escala semi-industrial, a produção do que viria a ser denominado Borracha Natural Líquida (LNR).

Por esse acordo o IRCA, detentor da tecnologia, recebeu uma contribuição especial da República Federal da Alemanha para executar o projeto. Foi instalada, então, na Costa do Marfim - país produtor de borracha, uma usina piloto para a produção de LNR a partir do látex do campo (apenas preservado), pois os resultados anteriores se referiam a látex concentrado. Além da produção de LNR, o projeto englobava ainda a pesquisa de utilização potencial do produto e aplicação industrial correspondente, pesquisa de derivados com potencial de aplicação industrial e estudo econômico da rentabilidade do processo.

O projeto, iniciado em abril de 1985, foi concluido em dezembro do mesmo ano e, para a divulgação dos resultados, foi organizada uma conferência internacional para a qual foram convidados profissionais atuantes na área de Química e Tecnologia da Borracha de diversos países.

Atendendo então, a um convite especial feito pela UNIDO, nos deslocamos para Abidjan, Costa do Marfim, no período de 16 a 25 de janeiro próximo passado, com a finalidade de assistir a conferência.

2. A CONFERÊNCIA INTERNACIONAL SOBRE BORRACHA NATURAL LÍQUIDA (LNR)

A Conferência foi realizada em Abidjan no período de 20 a 24 de janeiro e teve por finalidade, além da divulgação dos resultados do projeto, de colher também a opinião de todos os participantes convidados sobre o projeto e seus resultados e, principalmente, sobre o produto. O evento foi organizado pelo IRRDB e UNIDO e teve como participantes convidados, os profissio

nais a seguir relacionados:

Convidados da UNIDO:

Dr. S. Budiman	- Indonésia
Dr. L.M.K. Tillekeratne	- Sri Lanka
Dr. G.M. Bristow	- MRPRA
Dr. P.W.Allen	- MRPRA/IRRDB
Dr. J.C. Brosse	- França
Dr. Mei Tongxian	- China
Dr. Zainal bin Maidunny	- Malásia
Srª M.A. Neves	- EMBRAPA/Brasil
Sr. Surasak Suttisok	- Tailândia

Convidados do IRCA/CIRAD:

Sr. R. de Padirac	- IRRDB/IRCA
Sr. H. de Livonnière	- IRCA
Sr. Banchi	- IRCA
Sr. Laigneau	- IRCA
Sr. J. Sainte Beuve	- IRCA
Sr. A. Lemoine	- IRCA
Sr. A. Allet Don	- IRCA
Sr. G. Boccaccio	- IRAP
Sr. J. Marteau	- IRAP
Sr. Youssef	- UNIDO
Dr. L. Mullins	- UNIDO
Sr. C. Montano	- Brasil
Sr. Nkouonkam	- Camarão
Sr. Lin Zutang	- China
Sr. Kuriakose	- Índia
Sr. Tran Thanlong	- Vietnam

A abertura e o encerramento oficial da Conferência foi efetuado pelo Sr. Ministro da Educação Nacional e da Pesquisa Científica da Costa do Marfim, na presença de personalidades locais, representantes da UNIDO, do IRRDB e da República Federal da Alemanha, dos convidados participantes e

de todo o pessoal do IRCA em serviço no país.

Toda a Conferência se realizou segundo o programa abaixo descrito:

2ª feira - 20/01/86

10:00hs - Abertura oficial da Conferência em presença do Ministro da Educação Nacional e da Pesquisa Científica, de personalidades locais e representantes das organizações convidadas e participantes do acordo.

- Discurso das autoridades políticas
- Discurso de abertura
- Designação dos presidentes das sessões
- Apresentação do projeto por H. de Livonnière

12:00hs - Aperitivos

13:00hs - Almoço

14:30hs - 1ª Sessão: Produção de LNR

- IRAP "Parâmetros da reação de despolimerização"
  G. Boccaccio e J.C. Brosse

- IRCA "Descrição e princípio de funcionamento da instalação piloto de produção de LNR"
  M. Sainte Beuve

- IRCA "Produção de borracha líquida na Costa do Marfim em escala piloto"
  A. Lemoine e A. Allet Don

17:30hs - Encerramento da sessão

3ª feira - 21/01/86

08:30hs - 2ª Sessão: Propriedades e aplicações de LNR

- IRAP "Aplicações potenciais e desenvolvimentos possíveis de LNR"
  J. Marteau

- MRPRA "Novas aplicações possíveis de LNR"
  G.M. Bristow

- IRRDB - "Aspectos econômicos de LNR: produção e mercado"
P.W.Allen

12:30hs - Almoço

14:30hs - 3ª Sessão: modificações químicas de LNR

- RRI "Preparação de LNR a partir de crepe por ação de raios solares"
L.M.K. Tillerelatne

- SAPH "Situação atual da cultura de Hevea na Costa do Marfim"
Sr. Bullet

- BRIEC "Perspectiva de utilização interna de borracha na Indonésia"
S. Budiman

17:30hs - Encerramento da sessão

4ª feira - 22/01/86

08:45 - 15:00hs - Visita a Estação Experimental e Usina Piloto de Produção de LNR do IRCA em Bimbresso

5ª feira - 23/01/86

08:30hs - 3ª Sessão (continuação): Modificações químicas de LNR

- China "Alguns aspectos sobre o desenvolvimento de LNR na China"
Mei Tongxian

- IRAP "Modificações químicas de LNR por cloro ou anidrido malêico"
G. Boccaccio

- IRAP "Perspectiva sobre o desenvolvimento de LNR quimicamente modificada"
J.C. Brosse

12:00hs - Almoço

16:30hs - Mesa redonda

- UNIDO Conclusão da conferência
M. Youssef

18:00hs - Coquetel de encerramento

6ª feira - 24/01/86

07:30 - 13:00hs - Visita a plantação industrial e usinas da SAPH em Bongo.

3. A BORRACHA NATURAL LÍQUIDA

Em plena era da automação, da computarização e do rápido progresso tecnológico, a tecnologia do processamento da borracha é ainda bastante primitiva. A natureza do produto em sua forma semi-sólida, impede a automatização dos processos de manufatura que, ainda hoje, requerem força bruta e equipamento pesado com alto consumo de energia. Para superar o problema seria necessário ter a borracha em nova forma física como pó, granulado ou líquido, capaz de ser manipulada como fluido.

Foi como tentativa de atender a essa necessidade que os químicos e tecnólogos franceses pesquisaram e conseguiram produzir a borracha natural líquida, a exemplo do que já estava sendo feito com a borracha sintética desde 1943.

O produto caracteriza-se por um peso molecular na faixa de 10.000 a 12.000, de cor mel escuro, com teor de nitrogênio de 0,7%, de cinza - 0,4% e de impurezas - 0,015%, viscosidade Brookfield 300.000 Cps a 25ºC e de uma excelente estabilidade a estocagem. Sua preparação é basicamente simples, envolvendo os princípios abaixo, tomando-se o esquema do desenho para melhor orientação (fig. 1):

O látex é inicialmente estabilizado com amônia, soda e sabão no tanque nº 1. A seguir é transferido para o reator de despolimerização (tanque nº 2), no qual são injetados fenilhidrazina e oxigênio do ar. Este é borbulhado na solução (80ℓ/mm) sob agitação mecânica e temperatura média de 65ºC durante 24 horas. A formação de espuma é controlada pela adição de agentes

PLANTA PILOTO PARA BORRACHA LÍQUIDA (LNR)

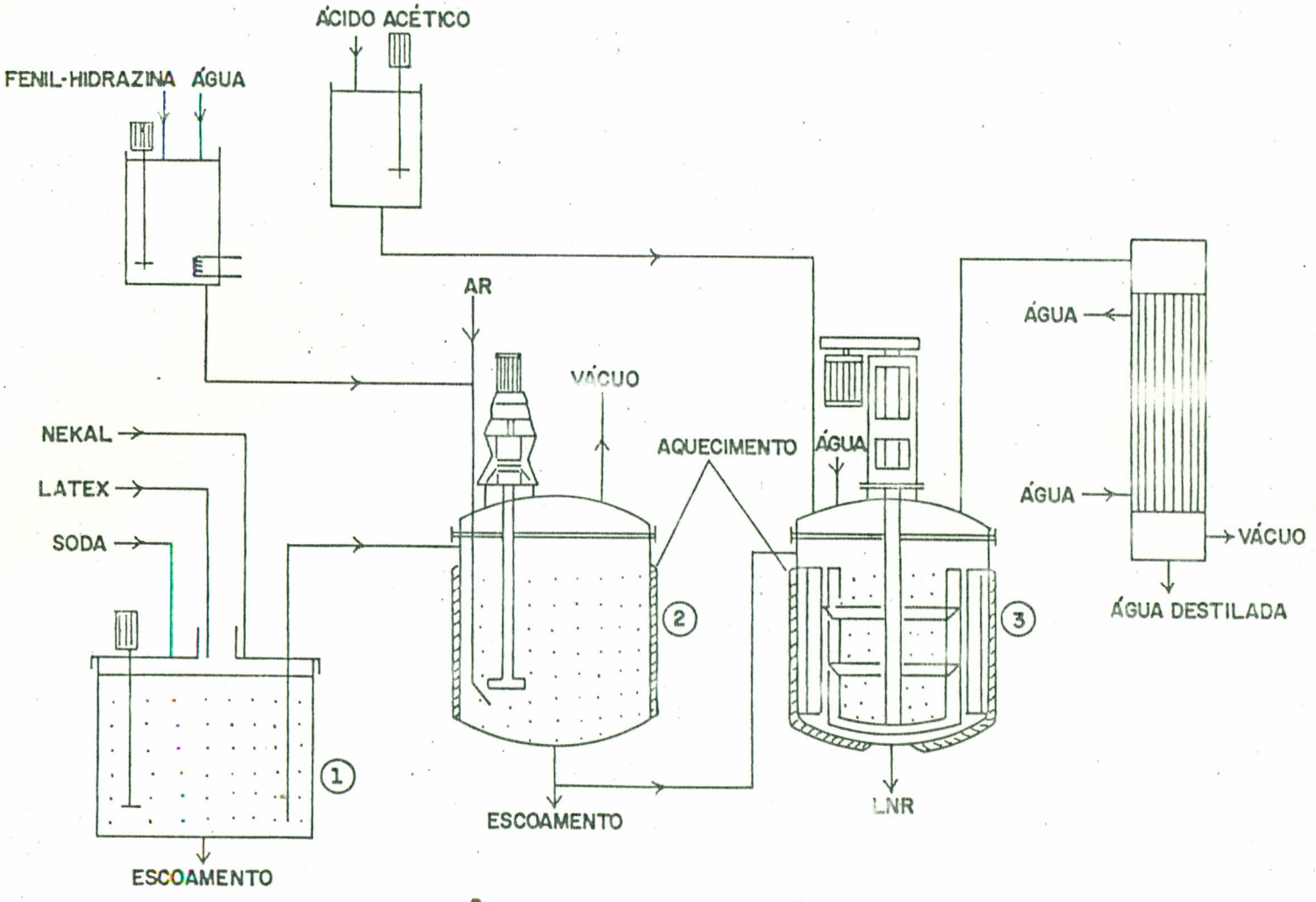


FIGURA 1

anti-espumantes especiais. Obtido o peso molecular desejado (teste de viscosidade) o látex é transferido para o reator nº 3 onde é coagulado com ácido acético ou fórmico. A mistura se separa numa fração sôro e num coágulo com consistência de "maionnaise". O sôro é descartado e o coágulo é lavado e, posteriormente, secado a vácuo por 10 horas. A borracha líquida obtida é então acondicionada em tambores de 200ℓ.

O produto, até o presente, tem um custo-produção relativamente alto, U$3,4/kg, em razão do alto preço do reagente fenilhidrazina, o que leva a uma inevitável restrição na aplicação industrial. Até o momento a borracha natural líquida encontra aplicação em:

- produção de artigos técnicos flexíveis e altamente elásticos como moulds
- como substituto de plasticizantes, sendo a borracha um produto vulcanizável
- como revestimento para produtos químicos em pó, melhorando a incorporação destes nas misturas de borracha natural
- como ligante para misturas de betume, tintas e abrasivos
- produção de adesivos, por sua força ligante.

É evidente que, reduzindo o custo produção, novas aplicações serão imputadas ao produto, principalmente nos processos de manufatura onde há no presente, necessidade do uso de borracha líquida como matéria prima.

Conseguido o produto a pesquisa agora se volta para a redução do custo-produção e para um estudo mais aprofundado sobre o desenvolvimento de novas aplicações que lhe assegurem um mercado mais amplo.

4. IRCA: ORGANIZAÇÃO E INFRA-ESTRUTURA

Fundado em 1956 na Costa do Marfim, o IRCA (Instituto de Pesquisa de Borracha da África), situa-se sob a tutela do Ministério da Educação Nacional e da Pesquisa Científica e funciona em acordo de cooperação, com Programa de Assistência Técnica Francesa para os países em desenvolvimento.

Localiza-se a 25 km de Abidjan consiste de um Centro de Pesquisa que engloba:

- Administração
- Departamento de Experimentação Agronômica
- Departamento de Química, Tecnologia e Usinagem
- Manutenção
- Unidade informática
- Produção Experimental

O staff consiste de 18 empregados sendo 13 pesquisadores, que tem 400 operários e técnicos sob sua responsabilidade.

As edificações compreendem (fig. 2)

. salas	200m²
. laboratórios	700m²
. casa de vegetação	150m²
. centro experimental de usinagem	150m²
. alojamentos	

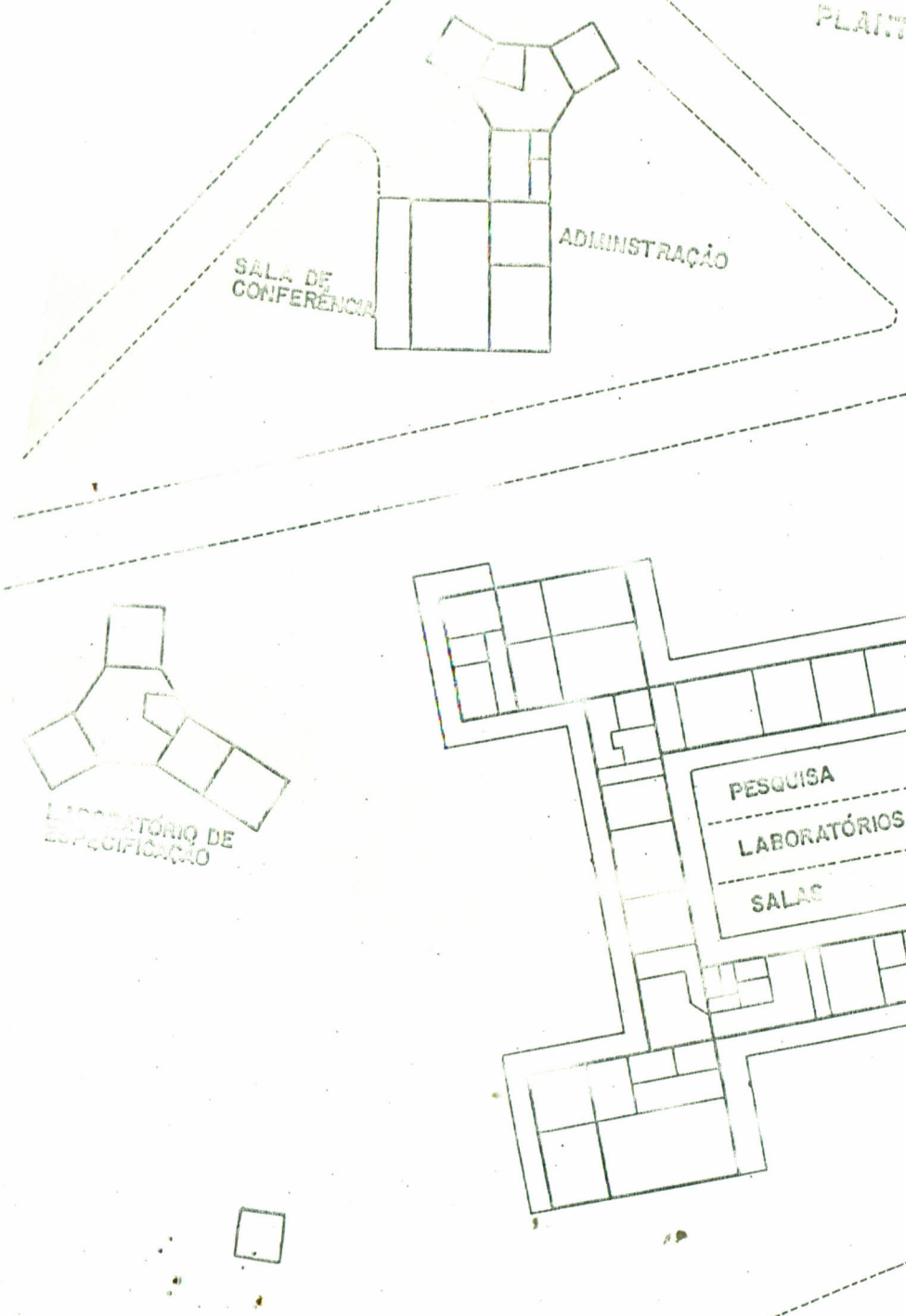
De uma área de 900m², 750ha estão plantados com seringueira, sendo de 600ha a área em produção.

4.1. O Departamento de Química, Tecnologia e Usinagem de Borracha

Composto de laboratórios, escritórios e um Centro Experimental de Usinagem, numa área total de 600m², O Departamento possui um staff de 3 pesquisadores e 20 técnicos de laboratórios e tem, como objetivos, o melhoramento e a diversificação da qualidade da borracha produzida na Costa do Marfim, a determinação de condições para redução dos custos de produção, a comercialização da produção sob especificação técnica e o desenvolvimento da indústria de transformação. Além disso, o Departamento tem sob sua responsabilidade a formação de profissionais destinados a indústria e a pesquisa.

Toda a borracha produzida na Costa do Marfim ($\pm$ 45.000t em 1985), é analisada e especificada no Laboratório de Especificações do Departamen

CENTRO DE PESQUISA DO IRCA EM BIMETESSO
PLANTAS DE LABORATÓRIOS E SALAS



to, num total aproximado de 9.000 amostras/ano, embora sua capacidade seja de 15.000 amostras/ano. Trabalham no Laboratório 6 técnicos químicos nível médio.

O Centro Experimental de Usinagem possui uma área de 150m² onde se localizam 2 máquinas crepadoras, um cortador rotatório, um moinho de martelo, um secador modelo IRCA, 2 estufas secadoras, um secador semi-industrial e uma unidade de coagulação e secagem, sendo estes dois últimos de modelo e fabricação do próprio IRCA.

O objetivo do Centro Experimental de Usinagem é a avaliação de novas tecnologias para as indústrias e o estudo de novas técnicas de processamento de borracha. O staff do Centro é composto de 1 pesquisador engenheiro mecânico e 3 técnicos nível médio.

5. CONCLUSÕES E SUGESTÕES

Mesmo contando com um tempo reduzido de estadia em Abidjan, foi possível contactar com todas as áreas do IRCA que nos interessavam, além de participar da Conferência sobre Borracha Natural Líquida, e ter as conclusões abaixo:

- o IRCA é um órgão de pesquisa e experimentação bem estruturado e voltado inteiramente para os problemas da cultura da seringueira e da tecnologia e química da borracha, com resultados que até o presente tem assegurado ao país uma produção crescente e um atendimento satisfatório as exigências da indústria.

- staff de pesquisadores é reduzido ao mínimo necessário para a realização das pesquisas e experimentos, mas o de pessoal de apoio é amplo e suficientemente especializado para atender as necessidades dos trabalhos.

- a Borracha Natural Líquida (LNR) é um produto com potencial futuro, na medida em que baixar seu custo produção e se tornar escasso o petróleo.

A viagem foi muito proveitosa e nos permitiu um contacto mais estreito com os pesquisadores franceses e ingleses principalmente, o que nos garan

te em parte sermos novamente convidados a participar de eventos similares. Desses contactos podemos sugerir que:

- a EMBRAPA dê maior apoio aos estágios e treinamentos de curta duração na França e Costa do Marfim aos pesquisadores envolvidos no PNP-Seringueira, principalmente nas áreas de Melhoramento Genético, Fisiologia, Química e Tecnologia.

- o CNPSD estude a possibilidade de se enviar para um treinamento de 6 semanas no Laboratório de Especificações e Centro Experimental de Usinagem do IRCA, os técnicos envolvidos com essas atividades no Laboratório de Tecnologia da Borracha do Centro.

- o CNPSD, pela sua chefia técnica, promova uma divulgação maior de suas atividades e seu corpo técnico junto a órgãos como o IRRDB e o IRCA, para que surjam oportunidades de participação em eventos como a Conferência sobre LNR, através de convites com custeio total de despesas, ou seja, com ônus limitado para a EMBRAPA.

6. ITINERÁRIO DE VIAGEM

15/01 - Saída de Manaus para Brasília às 14:00hs.
16/01 - Saída de Brasília para o Rio de Janeiro às 17:00hs e do Rio da Abidjan às 23:00hs.
17/01 - Chegada a Abidjan às 09:30hs (hora local)
25/01 - Saída de Abidjan para o Rio de Janeiro a 0:30hs, chegada ao Rio às 06:30hs e saída para Manaus às 10:30hs.

7. AGRADECIMENTOS

Além da Presidência da EMBRAPA pela permissão da viagem e a UNIDO pelo convite com que nos honrou para participar da Conferência, através do Dr. P.Allen - secretário do IRRDB, queremos agradecer de modo especial ao Dr. Afonso C.C.Valois e a Drª Zenete Peixoto França, sem a atuação eficiente dos quais essa oportunidade teria sido lamentavelmente perdida. Nosso agradecimento também ao Sr. Márcio M. Santos, Chefe Técnico do CNPSD, pelo seu apoio e orientação.

8. ANEXOS: RESUMOS DOS TRABALHOS APRESENTADOS NA CONFERÊNCIA

UNIDO - IRRDB CONFERENCE

January 20-24, 1986
ABIDJAN - IVORY COAST

LIQUID NATURAL RUBBER

DEPOLYMERIZATION REACTION

J.C. Brosse* and G. Boccaccio**

* Laboratoire de Chimie Organique Macromoléculaire-Faculté du Maine
** Institut de Recherche Appliquée sur les Polymères - I.R.A.P.

Le Mans - France

Thanks to the action of the oxydo-reducing air-phenylhydrazine couple, natural rubber is transformed in latex phase into low molecular weight polyisoprene. The different stages of the process as well as the incidence of the main parameters of the depolymerization reaction were studied in the laboratory. Some were examined in a small pilot unit preparing 20 kg of LNR. The process includes three main stages : stabilization depolymerization and operations of coagulation - washing - drying ; it can apply to both centrifuged and field latices. Studying the kinetics of depolymerization shows that for moderate temperatures (45 to 85° C), the two main parameters defining the state of depolymerization progress are phenylhydrazine amount and reaction duration. Optimizing the conditions of phenylhydrazine introduction did not, as expected, lead to a decrease in the amount of this fairly expensive reagent.

The molecular weight of the liquid natural rubbers obtained varies from 10,000 to 20,000 with a polymolecularity index ranging from 3 to 6. The 1-4 cis structure of the original polyisoprene is perfectly preserved ; the most numerous chain extremities are very likely of the phenylhydrazone type.

The three above-mentioned parameters, i.e. medium molecular weight, molecular distribution and chemical nature of chain extremities are determining as regards the properties of the products derived from natural rubber degradation. It is the in-depth study of each of them which will allow a complex degradation reaction involving multiple parameters to be controlled. Many authors have dealt with some aspects of this reaction in a systematic and fundamental way. Apparently, it is now admitted that the degradation of polyisoprene 1-4 cis chains involves hydroperoxide, cycloperoxide and epoxide structures resulting from the reaction of oxygen with phenylhydrazine and leads, through thermal decomposition, to the scission of macromolecular chains and achievement of carbonyl or carboxyl groups on the new extremities. Then the extremities can react with phenylhydrazine molecules whose initial concentration in the reaction medium is high and give phenylhydrazone extremities. Besides, the radical nature of the reaction kinetically subjected to the stages of initiation, propagation and ending translates into secondary reactions and obtainment of phenyl-carbinol or phenyl-ketone residues. This shows the degree of complexity this reaction is submitted to. A better understanding of the parameters controlling, it should allow the users of LNR to make it evolve in the direction desired.

UNIDO - IRRDB CONFERENCE

LIQUID NATURAL RUBBER

January 20-24, 1986

ABIDJAN - IVORY COAST

PROCESS PRINCIPLES OF PILOT PLANT FOR LIQUID NATURAL RUBBER.

J. Sainte Beuve

IRCA

Ivory Coast

The pilot plant is two-storied and spreads out at 20 m² wide and 6 m high. Il mainly consist of three reactors :

1.a/ Stabilisation

Field latex is stabilised with the help of soda (0,2%) and Nekal BX (1%) inside a 1 200 l fiber glass polypropylen tank and fitted out with an electric stirrer. This reaction lasts 2 hours at normal atmosphere and air pressure.
Then the latex is transferd under vacuum into the RO2 reactor.
Tube works used for transfert of the different liquids are stainless steel.

1.b/ Depolymerisation

The depolymerisation reactor RO2 is stainless steel fully insulated and has a total volume of 1 600 l. It is fitted out with an outer steel coil through which a heat tranfer liquid flows. This allows keeping a constant temperature of about 65°C during 24 hours.
A 80 KW electric boiler provides for calories. A stirrer fitted out with an electric engine of 1,5 KW works at 175 rpm owing to a reducer Poulibloc type.
Phenylhydrazin is preprared inside a heated stainless steel tank and introduced into the RO2 reactor with the help of peristaltic pump. A compressor ensures air bubbling at 80 l/mn during 24 hours.
After depolymerisation test, latex is transfered into the RO3 reactor under vacuum.

1.c/ Coagulation - drying

The RO3 reactor is similar to the one before except that it is fitted out with a different stirrer, more powerfull (5,5 KW) and at variable speed.

Coagulation is obtained by acetic acid (5%) addings, prepared in a polypropylen tank and introduced by a peristaltic pump. After decantation serums are drawn.

Three washing are following one another (400 L, 200 l and 200 l of water).

Drying is carried out under vacuum at saturating steam pressure, steams being condensed in a condensor (6 m^2). After 10 hours liquid rubber is drawn and poured into a 200 liters drum.

2. Effluent treatment

Liquid effluents are treated in an incinerator in which liquids are instantly atomized in a first combustion chamber. Then gaz are transfered into a second chamber where the temperature reaches 1 100°C.

3. Electrical generating set

We have gracefully been offered a 100 KWA electric generator by West Germany. This generator provides us with electric energy during the projet when going through power cuts (quite frequent in the Ivory Coast).

UNIDO - IRCOB CONFERENCE

LIQUID NATURAL RUBBER

January 20-24, 1986

ABIDJAN - IVORY COAST

PRODUCTION OF LIQUID NATURAL RUBBER AT PILOT PLANT SCALE, IN THE IVORY COAST

PRINCIPLE

A. Allet Don

IRCA

IVORY COAST

The liquid natural rubber pilot plant, installed on IRCA's site, at Bimbresso (Ivory Coast) produces a 200 kg batch of rubber per week, from roughly 700 l of latex.

The latex, from IRCA's plantation, is preserved in the field by addition of ammonia (4-5 g/l). This preservation allows a storage for several weeks. Before utilisation we add soda and soap to give the latex a good mechanical stability (specially at elevated temperature).

Transfer of latex between stabilisation tank and reactor is made by sucking under vacuum.

Depolymerisation reactor is equiped with a jacket for temperature control. The reaction takes place at 65°C for 24 hours and the kinetics is monitored by taking samples. A "quick test" gives the viscometer molecular weight of the rubber.

The air flow, an important parameter for the reaction, is controled by a needle valve. Phenylhydrazine is added, as a shot, at the beginning of the reaction.

Coagulation is done, after transfer in an other reactor, by addition of acid (acetic or formic) under smooth agitation. The serum is removed , after decantation, stored and destroyed by incineration.

After washing (three times) the coagulum is dried under vacuum for around 10 hours and the obtained rubber is poured into a drum by opening the reactor bottom valve.

UNIDO - RRDB CONFERENCE

LIQUID NATURAL RUBBER

January 20-24, 1986

ABIDJAN - IVORY COAST

PRODUCTION OF LIQUID NATURAL RUBBER AT PILOT PLANT SCALE, IN THE IVORY COAST.

PARAMETERS

Dr. Alain Lemoine

IRCA

IVORY COAST

Liquid natural rubber produced in the pilot plant is analysed in order to evaluate the production quality (level of impurities, residual rate of moisture) in addition we check the chemical parameters (i.e. molecular weight, viscosity) to characterize the obtained products.

Working at semi-industrial stage, we firstly have studied the production process reproducibility. The air flow entering the depolymerisation reactor, which seems to be the most important parameter concerning batch to batch variations, has been monitored and measured. Its reproduction during a series of batches give rubbers with same molecular weight and same viscosity.

Varying the phenylhydrazine amount it is possible to obtain a range of rubbers with viscometric molecular weight between 6 000 and 25 000, and on a reproducible way.

Depolymerisation trials under pressure are possible, but it seems that they do not have an important influence on reaction kinetics. The only advantage, at 1 bar, is the reduction of foam which allows a better control of air flow.

Coagulation is an important step during the production of liquid natural rubber. And the conditions in which it takes place (amount of acid, latex temperature, period) play a primordial role on the final rubber chemical parameters.

UNIDO - IRAP CONFERENCE

January 20-24, 1986
ABIDJAN - IVORY COAST

LIQUID NATURAL RUBBER

POTENTIAL APPLICATIONS OF LNR AND DEVELOPMENT WITH CUSTOMERS

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Institut de Recherche Appliquée sur les Polymères - IRAP

Le Mans - France

As the IRAP pilot unit gives access to sufficient amounts of LNR, technological studies have been undertaken in the laboratory to detect potential applications before customer prospecting. The following aspects have particularly been examined : formulation reinforcement and implementation, achievement of low hardness vulcanizates at moderate temperature, coating of ingredients used in rubber processing and use of LNR as a processing aid. Afterwards, contacts with customers aimed at inciting, determining and identifying needs for LNR. The objective was also to make the manufacturers contacted propose tests on a free basis. Owing to the results of the previous technological studies, the main industrial sectors for which the product was a priori regarded likely to be of interest to were the following : coating of vulcanization ingredients, rubber processing, adhesives and adhesive ribbons, paints and varnishes, cable manufacturing and waterproofness. However, it appeared quickly that it was necessary to adapt prospecting to better defined or new unexpected sectors, abandoning those which did not prove worth while or were more concerned by "second generation" products derived from LNR. The sectors of cable manufacturing, waterproofness and paints therefore were left aside. On the other hand, two new sectors were introduced : flexible moulds and ebonites. In addition, equipment manufacturers were contacted to determine the pumping possibilities of LNR and answer to the observations aroused by the difficult processing of the product on conventional equipment. A large number of firms were contacted and visited, corresponding to the following possible uses of LNR : reactive plasticizer and operating agent in rubber processing ; raw material of formulations for enduction, glues, adhesives and adhesive ribbons, mastics ; binding agent for abrasive grains and coating of vulcanization agents ; formulation element for cellular rubber, anti-corrosion coatings and low hardness vulcanizates used as flexible moulds. According to the sector of activity, the manufacturers' opinion has considerably varied but as part of their test campaign, around 1/4 of the firms which had already made a first estimate, wished to collaborate with IRAP in order to get a better understanding of the product. This occurred in the following sectors : coating, car rubber processing, shoe industry, enduction, adhesives, pourable compounds and abrasives.

Following this prospecting campaign and the technological works performed in cooperation with the manufacturers, we wish to mention the sectors where LNR is still of interest and tested, without being able to give any prediction regarding the future consumption of the product neither in France nor in Europe. These sectors are : tyre industry, cellular rubber, adhesive ribbons and some structural adhesives, moulding, and coating of vulcanization ingredients. However, as most manufacturers think LNR properties are average in comparison with its cost price, we believe it is appropriate that outlets should be searched for in the manufacturing area in developing countries.

UNIDO - IRRDB CONFERENCE

LIQUID NATURAL RUBBER

January 20-24, 1986

ABIDJAN - IVORY COAST

SOME POSSIBLE NEW APPLICATIONS FOR LIQUID NATURAL RUBBER

G. M. Bristow, A. G. Sears, M. A. Wheelans

- Tun Abdul Rasak Laboratory (MRPRA) -

- United Kingdom -

The traditional uses for liquid rubbers are well established. These are in encapsulation compounds, mastics, sealants and adhesives, applications which make use of the ability of the liquid polymer to flow often into complex shapes not readily achieved by normal moulding techniques. This paper however, describes attempts to use liquid natural rubber, LNR, in several more novel applications.

First, possibly because of its structural similarity to NR, LNR when added at 10-40 pphr to an NR compound produces a soft, easily processed material but with a greater green strength than results when conventional hydrocarbon oil process aids are used. This difference disappears after vulcanization, suggesting then most of the LNR does not covulcanize into the network. However, after oxidative aging which involves further crosslinking, vulcanizates containing LNR show an enhanced retention of tensile strength as compared to vulcanizates containing oil.

Second, the addition under appropriate conditions of 10 % LNR to a powdered rubber accelerator CBS provides a satisfactory anti-dusting coating. However, despite the reactive nature of this coating no evidence could be found of improved dispensability and hence compound homogeneity, even under adverse mixing conditions.

Third, established chemical techniques have been used to convert LNR into a substituted p-phenylene diamine potentially covulcanizable into a rubber network, and hence non-extractable during service. The material synthesized shows some evidence for attributes of this type.

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ECONOMIC ASPECTS OF LIQUID NATURAL RUBBER PRODUCTION AND MARKETS

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The new IRCA LNR production process achieves depolymerization by a "redox" system which is capable of achieving depolymerization at modest temperatures. This process is inherently "clean". An additional advantage of the new process is that the starting material is latex from the tree. These improvements might be expected to offer the opportunity of LNR production at lower cost than by the older routes. These advantages are unfortunately counterbalanced by the high cost of the reducing agent (phenylhydrazine). Analysis of the likely production cost for a hypothetical plant with a capacity of 1300 tonnes/year indicates that this cost would be around US $ 2.5 per kg.

The current main applications for LNR are those that require a moderately fluid castable polymer with useful adhesive qualities. Thus, LNR is used as a "hole filling" polymer (in sealants, cable jointing compositions, the fabrication of articles such as grinding wheels, paintbrushes, etc.) and in some adhesive applications. There is a good chance that the new LNR will be able to displace the older versions in applications such as these : it will not be more expensive and it is a better, cleaner material; and given appropriate promotion, there is a market of around 500 tonnes / year available. In an effort to reduce the selling price, attention should be paid to two features : (1) the possibility that a higher molecular weight (and therefore cheaper) LNR might be adequate for some applications, and (2) investigation of the use of cheaper redox systems.

Concerning new opportunities for LNR, one can only note some possibilities : in the production of coated chemicals for the rubber industry, and its use as a plasticizer for NR. The former does seem promising but the market is not large (eg about 100 tonnes/year for W. Europe). Use of LNR as a plasticizer for NR is an interesting concept because LNR might be expected to become vulcanized in with the main vulcanizate network. In fact, experiments suggest that only a small proportion of the LNR is so combined, and there are theoretical reasons why this should be so. Given this, and given the fact that LNR is at least five times as expensive as a process oil, we are doubtful that this is a viable application.

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STUDIES ON THE USE OF SOLAR ENERGY FOR THE PREPARATION OF LIQUID RUBBER

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This paper explain the use of solar energy in making liquid rubber out of dry crepe rubber in the presence of a photo activator. The liquid rubber obtained this way using nitro benzene as the photo activator has very good physical properties compared to other types of liquid rubber obtained by thermal means. However the toxicity of the unreacted nitrobenzene restrict the wide usage of this material in industry ; while the liquid rubber obtained by this method tends to harden on storage.

Both these defects have been successfully overcome in this project work by expoxidising the liquid rubber using a per acid to give an epoxy compound useful in fibre reinforcing industry.

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PROSPECTS OF DOMESTIC RUBBER USAGE IN INDONESIA

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The paper provides a brief overview of the inception and development of natural rubber industry in Indonesia, including manufacture of rubber goods.

Particular emphasis is given on the recent progress in rubber production and the potentials for an increase in domestic rubber usage due to the large Indonesian population with improving standard of living.

To intensify domestic consumption, it is thought that a substantial amount of rubber could be absorbed for the production of inexpensive latex foam sleeping matress, in combination with rubberized coconut coirs to accommodate the need of the medium and low income population.

Furthermore, this product can be fully manufactured by our small scale local industry, as it will not require any heavy machinery.

Concerning Liquid Natural Rubber (LNR), preliminary trials are being conducted to use LNR in slow-release formulations of pesticides and fertilizers. To minimize cost, LNR will be prepared from flatbark rubber which is derived from partially oxidized and contaminated earth scraps and tree lace. Depolymerization will be carried out through reaction with nitrobenzene under UV light. The obtained LNR will be subsequently mixed with the active ingredient and subjected to room temperature vulcanization. Controlled release of the active ingredient could be achieved through adjustment of compounding materials.

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SOME VIEWS ON THE DEVELOPMENT OF LIQUID NATURAL RUBBER IN CHINA

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The rubber market in China, natural and synthetic or rubber manufacturing industry is quite different from that of the other natural rubber producing countries.

Indeed China not only produces large quantity of natural rubber, 188,000 tons in 1984, but also of synthetic rubber, 170,000 tons in 1984. At the same time, China is one of the major consumers in the world : 550,000 tons per year. The consumption of natural rubber amounts to 65 % of the total consumptions.

The research and development of liquid rubbers, LNR particularly, in China is relatively backward, but at the moment they are still at trials laboratory production stage.

Two ways of development seem possible :

. rubber footwear industry :

China is a large rubber footwear producing country, with an annual production of 300,000,000 pairs ;

. coating :

the annual coating production in China is 612,000 tons out of this only 500 tons is elastomer based type.

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LIQUID NATURAL RUBBER

CHLORINE AND MALEIC ANHYDRID CHEMICAL MODIFICATIONS

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Liquid natural rubber has been used as a new basic polymer to study two chemical modifications : chlorination and maleic anhydrid fixation.

The final objective of chlorine modification is to obtain from LNR, chlorinated rubbers with properties close if not equal to those of the commercial products used in the fields of anti-corrosion paints and adhesives. The works mainly dealt, on the one hand, with the development in the laboratory of an operating method in solvent phase giving access in simple conditions to a chlorinated LNR possessing at least 65 to 68 % of chlorine and, on the other hand, with the study of the properties of the products obtained. It has been shown that supplying a catalysis by ultra-violet rays during the action of gaseous chlorine on liquid rubber in solution allowed the product desired to be obtained. As compared with high molecular weight natural rubber, the great solubility of LNR makes it possible to work with more concentrated rubber solutions without any degradation pre-treatment. The residual carbon tetrachlorid, viscosity in solution and stability of chlorinated LNR have been compared to those of the commercial products. Several additional chlorination tests carried out in latex phase did not prove promising, being the fixed chlorine content below 60 % and the polymers obtained insoluble.

Maleic anhydrid modification of liquid rubber aims at obtaining a new polymer possessing interesting adhesive properties. The two possible fixations of maleic anhydrid, i.e. radical and thermal fixations, have been applied to a LNR derived from centrifuged latex. Since it gave higher results, thermal modification was more fully examined. Modified polymers show cyclic succinic anhydrid groups and carboxylic acid functions resulting from cycle opening. It has been shown that the adhesive properties of modified LNR were maximum for a modification rate around 20 %. These properties have been estimated on aluminium/aluminium associations. The maximal shearing strength, of around 100 kg/cm^2, is highly satisfactory although lower by half than that of a performant structural glue of the epoxy type. Unfortunately, it is essential to use a solvent to process modified LNR.

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LIQUID NATURAL RUBBER

PRESENT SITUATION AND PROSPECTS

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Liquid Natural Rubber is obtained on production sites by an oxidation-reduction chemical treatment in latex phase, involving, apart from phenylhydrazine, no chemical compound other than stabilizers and above all requiring no organic solvent. The minutely studied process, from both the fundamental and application standpoints, allows 200 kg of liquid rubber per week to be obtained today in a pilot unit. According to the parameters of the chemical degradation reaction, it is possible to achieve rubbers with various molecular weights capable of covering a fairly wide range of applications. An in-depth study of the possible uses of the product itself is also given in another way.

In this paper, we shall limit ourselves to examining liquid rubber as a basic compound able to be subjected to subsequent chemical modifications and lead thus to new products with various applications. If the process used cannot control straight away the chemical nature of chain extremities and therefore LNR cannot be used as a macromolecular network precursor. On the other hand, liquid rubber macromolecular structure is of the perfectly regular 1-4 cis polyisoprene type. This fundamental characteristic can be taken advantage of to apply to this new component the already known chemistry of natural rubber, in order to generalise the conventional reactions of polydiene, because reaction process is easier owing to the liquid nature of this compound. As far as medium and long-term prospects are concerned, the point therefore is to consider liquid rubber, apart from its use as such, as a basic product able to be subjected to chemical modifications and lead to a new and very wide range of compounds some of which are studied in the laboratory or in the process of being estimated.