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# PREPARATION AND USES OF CYCLISED RUBBER AND OF CHLORINATED RUBBER

BY

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SUMMARY

*If cyclised rubber and chlorinated rubber could be produced by simple methods in the natural rubber (NR) producing countries, then they could have several important uses in these countries. The production of these derivatives by simple methods should considerably lower the prices from the rather high prices at which they are at present available, thus resulting in their increased world wide usage.*

*The simplest method for preparing cyclised rubber is by mixing 100 parts of NR with 8 parts of para toluene sulphonic acid and heating for several hours, at 140 °C. This method does not give a homogeneous product. Improvements made by us in preparing the raw rubber and by adding a phenolic antioxidant to the NR enabled a homogeneous cyclised rubber to be obtained in half an hour at 110 °C. Uses of cyclised rubber as a reinforcing filler, in paints and in printing inks are discussed.*

*The simplest method of preparing chlorinated rubber is from stabilised field latex and the chlorine generated* in situ *using sodium chlorate and concentrated hydrochloric acid. Modifications necessary to prepare soluble chlorinated rubber and some of its possible uses are discussed.*

## INTRODUCTION

Research and development on chemical derivatives of NR for export and for use in the producing countries are necessary for the continued prosperity of the NR plantation industry. It is true that even if such research is successful it may not be a major use for NR, but a small rubber producing country such as Sri Lanka with an annual NR production of approximately 150,000 tons is actively interested in looking into ways and means of getting the maximum foreign exchange earnings from her NR. Progress in the field of production of chemical derivatives of NR in the producing countries has been very slow. Self reinforcing rubbers in the form of cyclised rubber masterbatches and graft polymers especially those with methyl methacrylate are now being produced on a modest scale. The three important chemical derivatives of NR produced commercially by developed countries are chlorinated rubber, rubber hydrochloride and cyclised rubber. This paper discusses simple methods of preparation and some possible uses of cyclised rubber and of chlorinated rubber in the NR producing countries themselves.

## *CYCLISED RUBBER*

By suitable treatment the long straight molecular chains in NR may be joined together to form ring-like structures resulting in the formation of cyclised rubber. Cyclised rubber is a resin and the reaction occurs under the action of heat especially in the presence of acidic catalysts of the Friedel crafts type. Cyclised rubber can be prepared from solid rubber, rubber solutions or from latex. This paper discusses the preparation and uses of cyclised rubber from solid rubber and from latex.

*Preparation of cyclised rubber from solid rubber*

Fisher (1927) has shown that cyclised rubber can be produced by mixing 10% of para toluene sulphonic acid to solid rubber, sheeting it and then heating the sheets for several hours at 125-135 °C. However, the product obtained was not homogeneous. Jannsen (1956) has stated that, with the normal grade of rubber cyclisation was about 10 times slower than with the low protein grades of rubber and that substantial cyclisation took place in the latter at 150 °C in about 30 min. Even in this method the cyclised rubber product obtained was not homogeneous with a medium overall degree of cyclisation. Mast (1968) states that for the cyclisation of undiluted rubber, a catalyst is mixed into the rubber on a mill and the mixture is heated in the oven for several hours at 150 °C. He also states that the reaction is strongly exothermic and the temperature may rise to 250 °C in a few minutes.

*Preparation of cyclised rubber from latex*

The development of the commercial production of cyclised rubber directly from latex on the plantations took place between 1952-1956 (Edwards, 1955). The process involves the addition of 98% commercial sulphuric acid to stabilized centrifuged latex with continuous stirring, until the concentration of sulphuric acid in the latex is about 80% and heating over a water bath for approximately 2 h. On coagulation by pouring the mixture into a considerable excess of boiling water, cyclised rubber is obtained. In practice, the treated and untreated latices are mixed prior to coagulation and a cyclised rubber masterbatch is obtained.

## *CHLORINATED RUBBER*

*Preparation of chlorinated rubber*

The method for the preparation of chlorinated rubber which is used on a substantial scale in commercial production is the direct chlorination of rubber in an inert solvent *e.g.* carbon tetrachloride, at temperatures around 80 °C. In order to avoid gelation during chlorination and to obtain products of a sufficiently low viscosity to be practically useful, the rubber is usually broken down considerably, normally by milling before putting it into solution (Bloomfield, 1961).

Chlorinated rubber has also been prepared directly from latex (Baker, 1938). The chlorination of latex can be accomplished directly at temperatures around 20-30 °C, provided that the latex is first stabilized by means of a non ionic or by means of a combination of a non ionic and a cationic stabilizer. A strongly acid medium is distinctly advantageous in avoiding incidental addition of hypochlorous acid. This can be achieved if the serum is brought to an acid concentration of 8 N HCl. Chlorinated rubber has been prepared by adding a chlorate solution to latex stabilized with HCl, whereupon the chlorine generated *in situ* reacts rapidly with the rubber. The preparation of chlorinated rubber from latex has not reached the scale of commercial production. This method usually gave a rather insoluble product and only by degradation of the latex have soluble products been obtained using promoted oxidation, BP 390,097.

The commercial production of soluble chlorinated rubber from suitably stabilized field latex would be of great value to the natural rubber producing countries. By soluble chlorinated rubber is understood a chlorinated rubber which is completely soluble in the conventional solvents of the paint and the lacquer industry, *e.g.* aromatic hydrocarbons, chlorinated hydrocarbons, esters and ketones. This solubility is desirable, *e.g.* for working up the chlorinated rubber into paints and lacquers.

The advantages of chlorinating latex rather than a solution of rubber are that the initial high molecular weight of rubber is substantially conserved, a higher rubber concentration may be employed and heat development is less of a problem. The production of a high-quality chlorinated rubber calls for relatively great capital expenditure and special know-how and has thus become concentrated with only a few producers. This paper contains preliminary investigations carried out by us to produce chlorinated rubber for use in Sri Lanka and if we can achieve a high quality product to export it.

## EXPERIMENTAL

### *CYCLISED RUBBER*

*Preparation of cyclised rubber from solid rubber*

A practical simple method of manufacturing cyclised rubber is by reacting low protein rubber with para-toluene sulphonic acid. The low protein rubber commercially available has been prepared by the method developed in Malaysia (Anon, 1956), in which the latex is first centrifuged, then diluted to 7.5% d.r.c. and coagulated, creped and dried. This low protein crepe has the defect that the rubber obtained from it is very prone to oxidation because of the leaching by the ammonia of alkali soluble antioxidants, *e.g.* tocotrienols present in the rubber particles (Nadarajah *et al.*, 1972). This defect does not occur with papain deproteinised crepe (Nadarajah *et al.*, 1973), and the use of this as the raw rubber opens up a simple method for the manufacture of cyclised rubber and is the main basis for a Sri Lanka Patent application (Nadarajah *et al.*, 1972). It was also noted that the yellow fraction is not easily cyclised. Verhaar (1954), and Homans & Van Gils (1948) have stated that fresh latex is characterised by the presence of viscoids of greatly varying size. It is these viscoids that coagulate in the yellow fraction and they contain a large amount of non rubber substances. Hence, it is necessary to remove the yellow fraction before cyclisation. The method of preparing cyclised rubber was as follows:

1,000 g of field latex to which no anticoagulant such as ammonia, formaldehyde or sodium sulphite were added were taken and the yellow fraction was removed, as both formaldehyde and sodium sulphite were found to act as inhibitors of cyclisation. The procedure of removing the yellow fraction is as follows:

Field latex is standardised at 2 lb per gal by the addition of water, the latex is stirred briskly for two 20 min periods, with an interval of about 10-15 min midway. While stirring, it will be necessary to dip one's hand into the latex occasionally in order to ascertain whether the yellow particles are forming. If at the end of the period of mixing the particles of yellow rubber are not visible on the surface and on the palm of the hand, stirring should be continued for about another half an hour. If the particles of yellow rubber in the latex are visible on the palm of the hand, the latex is allowed to remain undisturbed for about 10 min and is then stirred gently until the yellow particles form into clots. The fraction is removed and the latex is strained through a 60 mesh sieve and 0.5 g papain which was made into a slurry with some water and then made up to about 100 ml with water, were added to the strained latex. The coagulum was rolled on the same day through a grooved roller (3 times) and a smooth roller (once) under a copious spray of water and the thin lace dried in a drying tower. 100 g of this rubber were taken, masticated and then 8 g of paratoluenesulphonic acid mixed into it. The rubber was sheeted and heated at 100—120 °C in an aluminium tray in an oven for half an hour. Cyclisation commenced in 15 min and was over in half an hour. Chemicals such as sodium bisulphite inhibit the cyclisation reaction and should not be used in the preparation of the deproteinised crepe.

D'Ianni *et al.* (1946) have shown that the type of antioxidant used to protect polyisoprene was found to have a considerable effect on the colour of the isomerised product. They state that if PBN is used the product is cream coloured and the solutions are brown, and that if a non discolouring antioxidant is used, the rubber and resulting cyclised product are considerably lighter in colour. They also state that at least some of the antioxidant passes unchanged through the isomerisation process and is still available to protect the product against oxidation as evidenced by the fact that antioxidant free rubber gives an aliphatic solvent insoluble cyclised product. Our experiments on the use of PBN and 2,6 ditertiary butyl para cresol at one and two phr respectively confirmed the above findings in that light coloured aliphatic solvent soluble cyclised rubber was obtained.

The cyclised rubber was powdered by passing through a mixing mill, and could be milled by further passes through the mixing mill to reduce its molecular weight. It is suspended in water and neutralised with sodium carbonate or with ammonia solution. The suspension was separated by decantation, washed with water, separated and dried. If rubber seed oil alkyd at 5 to 10 phr is added to the rubber before cyclisation, a lighter coloured cyclised rubber is obtained.

*Analysis of cyclised rubber*

Samples of cyclised rubber prepared by us were analysed (Mendis 1973) at the University of Technology, Loughborough, England. Differential thermal analysis showed that they had a glass transition temperature around 30 °C and a softening point less than 100 °C. The infra red spectrum revealed a loss of unsaturation of C=C stretching at 1665 $cm^{-1}$ as compared to NR. The band at 830 $cm^{-1}$ was absent in the cyclised rubber samples denoting a loss of trialkyl double bonds present in NR. The infra red spectrum showed a definite IR band at 888 $cm^{-1}$. This band is attributed to exocyclic $>C=CH_2$ was and indicates that the cyclosity is low and is less than 3 (Agnihotri *et al.*, 1972) and probably between 2 and 3.

## *CHLORINATED RUBBER*

*Preparation of chlorinated rubber*

Chlorinated rubber is prepared from latex by the method suggested by Rajasingham *et al.* (1972). The cheapest and most efficient stabilizer for the NR field latex is formaldehyde at a concentration of 0.3% and Vulcastab LW at 0.75% on the latex, respectively. It was found that the solubility of the chlorinated rubber produced is a clonal factor, *e. g.* field latex from clones PB 86 and RRIM 513 gave a soluble chlorinated rubber, whilst that from RRIC 7 gave an insoluble chlorinated rubber. It is possible to obtain soluble chlorinated rubber from latex of clone RRIC 7 by the addition of an oxidation catalyst, *e. g.* cumene hydroperoxide (0.05%) or xylyl mercaptan (0.2%) or mercaptobenzothiazole (0.4%) or boric acid (0.4%) to the latex before chlorination.

It may be mentioned that benzoyl peroxide has been used as a depolymerising agent for NR in the preparation of chlorinated rubber from solution (Stern, 1967). The amount of benzoyl peroxide is carefully controlled and determines the grade or viscosity of the final product. The use of benzoyl peroxide has been found more economical and convenient than mastication of rubber.

The method of preparation of chlorinated rubber from field latex was to add solutions of 25% formaldehyde and 10% diammonium hydrogen phosphate to it to bring their concentrations up to 0.3% and 0.15%, respectively of the latex which is then allowed to stand for 24 h. The magnesium present in the latex precipitates as a sludge, the supernatent latex is decanted and to it is added a non ionic stabilizer, *e.g.* Vulcastab LW at 0.75% on the latex. This latex can be stored for several months before use and when required a 10% RPA3 (xylyl mercaptan) emulsion is added to bring the concentration to 0.2% on the latex. This is allowed to stand for 1 h and concentrated HCl is added at once at the rate 330 ml per 1000 ml of latex with vigorous stirring. Sodium chlorate solution is then added very slowly at the rate of 135 g solid chlorate per 1000 ml of latex. During the addition of the chlorate, the latex has to be stirred continuously while cooling the reaction vessel. The cooling is very important as the temperature tends to rise as the reaction proceeds. Cooling can be done by circulating cold water around the reaction vessel or by introducing cooling coils inside the reaction vessel. After completing the addition of the chlorate, the resulting mixture, is left overnight in the cooling bath for the powder to form. This powder is then filtered washed, neutralised and dried at a temperature below 50 °C.

A modified method for preparing soluble chlorinated rubber from NR latex is that described by Kirubakaran & Jayasinghe (1973). Field latex is stabilized with formaldehyde at 0.3% and Vulcastab LW at 0.75% and oxidation catalysts *e.g.* RPA 3 or cumene hydroperoxide added. Rubber solvents such as toluene, benzene or carbon tetrachloride are added at 5 to 10% on the latex, stirred well and kept for about 30 min. Concentrated hydrochloric acid is then added with good stirring and then the potassium chlorate solution is slowly added with stirring. The mixture is allowed to stand overnight and the powder of chlorinated rubber is filtered and dried. This method has the advantage that no cooling is required and no pronounced offensive odour of chlorine is noticeable during its preparation.

The dry powder is further ground in a ball mill. The viscosity in cps of the chlorinated rubber measured on a 20% solution of toluene : butanol, 95:5 at 30 °C in the Hoeppler Viscometer was 30. Chlorinated rubber spontaneously splits off minute quantities of hydrogen chloride, hence it has to be stabilized. A simple method of stabilization is to mix zinc oxide or finely powdered sodium carbonate at 3% into the chlorinated rubber. The incorporation of an epoxy compound, (*e. g.* Bayer Levepex 4020) improves the stabilization.

## *USES OF CYCLISED RUBBER AND OF CHLORINATED RUBBER*

### *Use of cyclised rubber made from latex*

*Injection moulding*: The use of cyclised rubber in injection moulding was investigated. Cyclised rubber masterbatch 90:10 which is a powder was found suitable for use in injection moulding. However, it had a tendency to degrade and to give an offensive smell during the injection moulding process. Better results were obtained when methyl methacrylate (MMA) grafted latex (25% MMA) was used in preparing the 90:10 masterbatch (Amarapathy *et al.*, 1972). This masterbatch could be injection moulded at a lower temperature, but the results are not satisfactory enough to consider commercial utilisation of this material.

*Emulsion paints*: An important use of cyclised rubber made from latex is in emulsion paints. The latices used in emulsion paints have been exclusively of the synthetic types. Nadarajah & Ganeshasunderam (1969) have discussed the use of MG latex in emulsion paints and stated that its quality is inferior to emulsion paints made from synthetic latices. Mendis & Nadarajah, (1971) have stated that the quality of MG latex emulsion paints could be considerably improved by blending with at least half its weight of synthetic latices. Narangoda & Nadarajah, (1973) have found that cyclised rubber masterbatch 90:10 where MG latex (25% MMA) was used in preparing the masterbatch was as good as synthetic latices for use in emulsion paints.

*Reinforcing filler*: Cyclised rubber masterbatch (50:50) was made in Malaysia as a reinforcing filler, but its production has declined owing to its inability to compete in prices with the high styrene resins.

*Uses of cyclised rubber from solid rubber*

*Organic reinforcing resin for NR*: An important use of cyclised rubber is as a reinforcing resin in rubber compounding. The first reinforcing resin from rubber to appear on the market was cyclised rubber prepared in solution. During the last War this product was superseded by the synthetic "high styrene resins" which have captured a large portion of the sole and heel market. Since the War, several attempts have been made to re-introduce cheaper forms of cyclised rubber. A high degree of cyclisation (Jannsen, 1956) of over 70% is required for the use of cyclised rubber as a reinforcing resin.

Cyclised rubber prepared by using para toluene sulphonic acid as the cyclising agent, was successfully used as a replacement for imported high styrene resin on an experimental scale, in a shoe sole formulation at Bata Shoe Company Ltd., Sri Lanka. A typical formula for a shoe sole application would consist of 70 parts of rubber, and 30 parts of cyclised rubber with white filler and normal amounts of vulcanising ingredients. Cyclised rubber must be milled into dry rubber at a temperature above its softening point and be mechanically dispersed and mixed as much as possible during the milling. Cyclised rubber imparts some of its stiffness to the rubber and should not be considered as real reinforcing agents, but rather as polyblends.

As a reinforcing filler cyclised rubber can be used in the manufacture of shock resistant plastics. A typical compound would consist of 70 parts of cyclised rubber and 30 parts of rubber as a plasticiser to decrease the brittle point with the normal amount of fillers and vulcanising agents.

Cyclised rubber in solution has been used as an ingredient in anti-corrosion finishes resistant to water and to chemicals and in printing inks. Neutralisation of traces of acid in solution is effected by introducing anhydrous sodium carbonate which is first made into a slurry with a little of the reaction product and then stirred into the hot bulk. Settling of suspended matter is facilitated by keeping the mixture warm. Gaseous ammonia may also be used.

Cyclised rubber finds wide use in smooth finishes particularly where brush application is required or where the paint has to be applied in an enclosed space, advantage being taken of its solubility in white spirit. A cheap plastic coating for coconut shells would be of great value in Sri Lanka in sole crepe, pale crepe, centrifuged latex and new process rubber manufacture. The plastic coating would not only reduce coagulation of latex in the field but also contributes to greater cleanliness. An important local resin

which could be manufactured in Sri Lanka for use in paints for coating of coconut shells for use in the plantation rubber industry is plasticised cyclised rubber in white spirit. Locally available rubber seed oil alkyd can be used as a plasticiser at 10% on cyclised rubber.

It is estimated that 50 lb of rubber is upgraded to Grade I crepe per acre per annum (Mendis & Nadarajah, 1971). If the cost of the paint is Rs. 23/- per gal then the cost of treatment per shell is -/05 cts and the nett benefit per annum per acre to producer is Rs. 5/50 (-/25 cts/lb of rubber taken as the price differential between crepe No. 1 and scrap and Rs. 7/- as cost of treating shells).

The most important feature in the use of treated shells in pale crepe manufacture would be the additional foreign exchange that would be earned. If pale crepe production is taken at 42,000 tons per yr, the additional availability of Grade I pale crepe is 5% of this, which is 2,100 tons. At a price differential of -/25 cts, additional foreign exchange earning would be about a million rupees. The local cost of raw materials used to cost the coconut shells will be well below this amount and the foreign exchange costs about 1/10 of this amount.

*Uses of chlorinated rubber*

The application of chlorinated rubber (NRPRA, Technical Information Sheet No. 16) are in protective coatings especially where resistance to chemicals or corrosive atmospheres is required, in traffic paint on roads, in adhesives, in printing inks, in paper coating and in textile finishes. Chlorinated rubber paint can be successfully applied on metal, on concrete or on asbestos cement by brushing or by spraying and is used on applications such as finishes on drinking water tanks, swimming pool finishes and in floor finishes. Contact adhesives can be made from chlorinated rubber, the ingredients being natural rubber, chlorinated rubber, Rosin, solvent, magnesium oxide, zinc oxide and Plasticiser. It may be mentioned that chlorinated rubber can be used in emulsion paints. Satisfactory emulsions can be made out of chlorinated rubber, by taking a solution of chlorinated rubber in toluene, introducing it into water along with emulsifying agents (Emulsifier W and Emulpher O) and emulsifying with a high speed stirrer. The composition is then ground with an aqueous pigment paste. Such emulsions can be freely thinned with water and they have a good shelf life. Finishes of these emulsions give good results on concrete, asbestos cement or asphalt surfaces.

## DISCUSSION

Mast (1968) states that for cyclisation, the rubber to which a catalyst is added is heated in an oven for several hours at 150 °C. Our process is for fractionating NR latex to which no other chemicals had been added, for coagulating the white latex with papain, and cyclising the crepe obtained with para toluene sulphonic acid in the presence of an antioxidant. In this process cyclisation occurs within half an hour at 110 °C, the temperature does not rise unduly high and a homogeneous cyclised product is obtained. Mast (1968) states the price of cyclised rubber is 1.10 to 1.40 US $ a pound. Cyclised rubber could be produced by the above method at below ⅓ the above price.

Cyclised rubber is soluble in aliphatics and this has led to its adoption in a much wider range of paints and printing inks than can be made with chlorinated rubber which is soluble only in solvent blends rich in aromatic hydrocarbons. The viscosity of cyclised rubber dissolved in aromatics or aliphatics is lower than that of chlorinated rubber and

therefore it is easier to make paints having a high solids content and greater build using cyclised rubber. A 30 to 35% solution of cyclised rubber in white spirit has a consistency suitable for brush application. Paints based on cyclised rubber can be formulated to resist quite high temperatures, much higher than with chlorinated rubber which begins to break down rapidly above 140 °C (Worsdall, 1951).

Chlorinated rubber may be considered superior to cyclised rubber as it can be used if suitably plasticised against acids and strong alkali solutions. However, both chlorinated and cyclised rubber can be used in finishes expected to meet heavy chemical exposure. Chlorinated rubber and cyclised rubber are compatible with long oil alkyd resins, *e. g.* long rubber seed oil alkyd resins. The optimum proportions of chlorinated rubber and alkyd are approximately 1:1 to 1:2, though the addition of small amounts 5 to 30% of chlorinated rubber or cyclised rubber to long oil alkyd resin gives a paint which dries faster and gives a better finish. The paint includes glossy, flat decoratives, and the floor paints. Resistance of the alkyd resin to water, steam, detergents and alkalies and also its flow is improved by this addition. In conclusion it may be stated that chlorinated rubber is one of the development projects in Sri Lanka Five Year Plan (1962-1967) and priority is being given to this promising project.

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