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USE OF NATURAL RUBBER LATEX IN LEATHER FINISHING*

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SUMMARY

This paper describes a method whereby modified natural rubber (NR) latex can be used in leather finishing. It not only acts as an import substitute, but can even improve the important property of rubfastness. Pending further research work, a 50% substitution of the imported synthetic binders by methylmethacrylate-grafted copolymer NR latex, for finishing embossed and lining leather is recommended.

INTRODUCTION

There are several new processes that are used in other countries for finishing of leather but they have been patented. Hence their use in Ceylon would entail not only the payment of royalty in foreign exchange, but also paying in foreign exchange for the materials to be used in these processes. In view of the tight foreign exchange position in this country, studies were undertaken on the feasibility of using NR latex in leather finishes. This paper presents the results of the studies carried out and shows that the use of NR, under certain conditions, can be superior to the synthetic latices used at the Ceylon Leather Products Corporation. No other country in the world has done work on the use of modified NR latex in leather finishes. Therefore a patent has been filed for the use of modified NR latex in finishing leather.

In the finishing of leather, pigments are necessary to cover the leather surface and to obtain the desired shades. Pigments do not stick to the leather surface and a binder is necessary to fix the pigment on the leather surface. Polymers in latex form are being used as binders in leather finishing and they can be classified into two groups, namely protein binders and thermoplastic resin binders. The resin latices used in finishing leather are almost exclusively of the synthetic types obtained by copolymerization of monomers such as methyl, ethyl and butyl acrylates, methyl methacrylate, styrene, butadiene, acrylonitriles, etc. Homopolymers of methyl methacrylates and of styrene are hard solids and cannot be used as binders in leather finishing owing to their poor flexing properties. Poly-acrylates and copolymers and styrene-butadiene, methyl methacrylate-butadiene, acrylonitrile-butadiene are soft rubbery resins at normal temperatures and are most suitable for leather finishes.

In Ceylon, the common type of high polymer that can be obtained in latex form is natural rubber latex which is a linear homopolymer of cis-1, 4-isoprene. In contrast to synthetic acrylate copolymer binders, natural rubber is a soft high polymer and only small proportions (not more than 10%) can be used with other synthetic binders in the finishing of leather. The property of rubfastness of leather which had been finished using only NR latex is very poor and the rubbery coat peals off indicating poor adherance to the leather surface.

The aim of our research project is to produce somewhat hard resins from NR latex comparable with the imported binders. As mentioned earlier, homopolymers of styrene and methyl methacrylates are hard resins whereas natural cis-1, 4-polyisoprene is a soft high polymer. By introducing methyl methacrylate polymer chains

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into the rubber particle by graft copolymerization a product was obtained which is comparable with the synthetic leather binders (Nadarajah & Ganeshasunderam, 1969).

Methyl methacrylate-grafting of NR latex is a very easy process and the polymerization takes place at room temperature (Muthurajah, 1964). The temperature of the reaction mixture rises by about 5°C during the polymerization reaction giving a product in which long homopolymer chains of MMA are directly attached to the methylene carbon atoms of polyisoprene.

In the graft copolymerization operation, an emulsion of cumene hydroperoxide and methyl methacrylate is made in water using ammonia and oleic acid as emulsifying agents and added to the field latex with constant stirring and the stirring is continued for a further 30 min to ensure thorough mixing of MMA with NR latex. Tetra ethylene pentamine is then added to initiate the reaction. Methyl methacrylate and cumene hydroperoxide migrate into the rubber particles and graft copolymerization takes place within the rubber particles. The degree of graft copolymerization can be varied by changing the proportion of MMA. However a small amount of free homopolymer of MMA is also formed during the grafting reaction. Provided substantial proportions of stabilizing soaps are avoided, polymerization takes place entirely within the rubber particles and no separate polymer particles are formed. Of the total poly (methyl methacrylate) formed only about half is grafted to the rubber.

EXPERIMENTAL

Investigations were carried out on the film-forming property of graft polymerized latex. The latex samples dried into soft films with up to 30% of graft copolymerization but beyond this, the latex produced somewhat cracky films (Andrews & Turner, 1960; Allen, 1963).

The rubfastness property of leather that has been finished using MMA-grafted copolymerized NR latex was also investigated and the results obtained were promising. In these experiments rubfastness property of leather finished with the synthetic binders and the MMA-grafted copolymerized NR latex was compared using the chialet rubfastness apparatus. It was found that the rubfastness property of unmodified natural rubber latex is very low, but it could be increased by blending with synthetic binders (Fig. 1).

It was found that the graft copolymer formation of NR latex with methyl methacrylate has a positive influence on rubfastness property and it increases with an increase in the percentage of grafting. By graft-copolymerizing upto 30-35% MMA into rubber a product is obtained which is equivalent in rubfastness property to the synthetic binders previously used, *e.g.* corial binder K 50. By graft copolymerizing 40% MMA into rubber latex a product is obtained which is about 50% superior to this synthetic binder in rubfastness (Fig. 2).

It was also found that rubfastness property of the synthetic binders could be further improved by blending with graft copolymerized NR latex (Fig. 1). This improvement of rubfastness property can be considered due to a glazing effect of the graft copolymerized NR latex.

However, there is a limitation to the percentage of graft copolymerization. The graft copolymerization of more than 30% MMA has a bad influence on the film-forming property of NR latex but it was observed that even 40% graft copolymerized NR latex could be used as a binder for the leather finishing without any bad effect on leather. The reinforcement effect of pigments, dyes and other ingredients incorporated into the latex in finishing operations improves the film-forming property

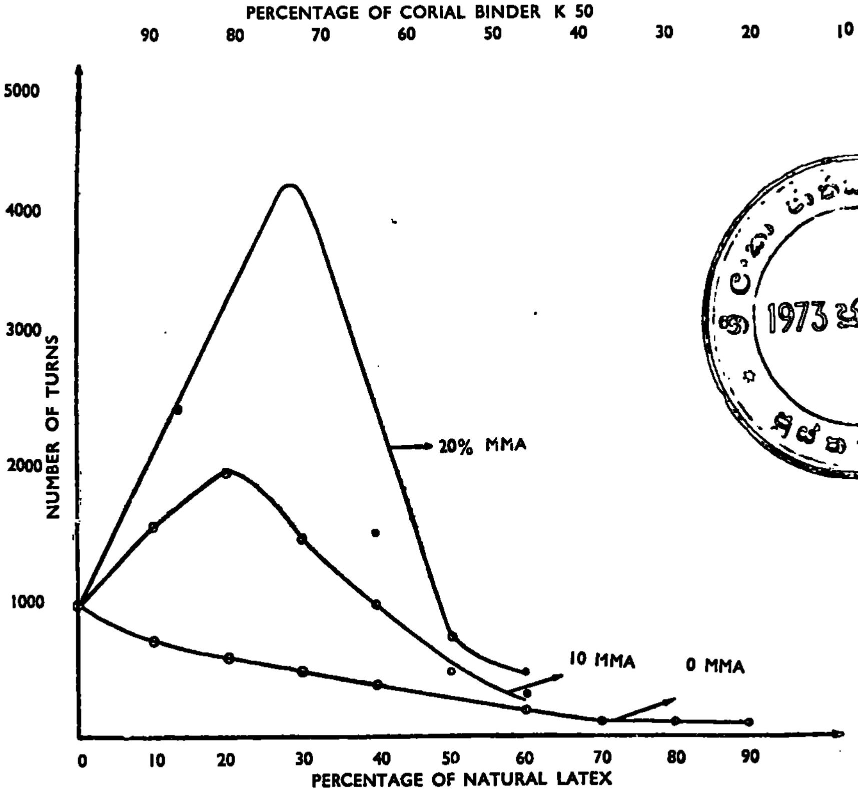

Fig. 1. Variations of rubfastness of leathers which have been finished with corial binder K50 and different grafted natural rubber latex.

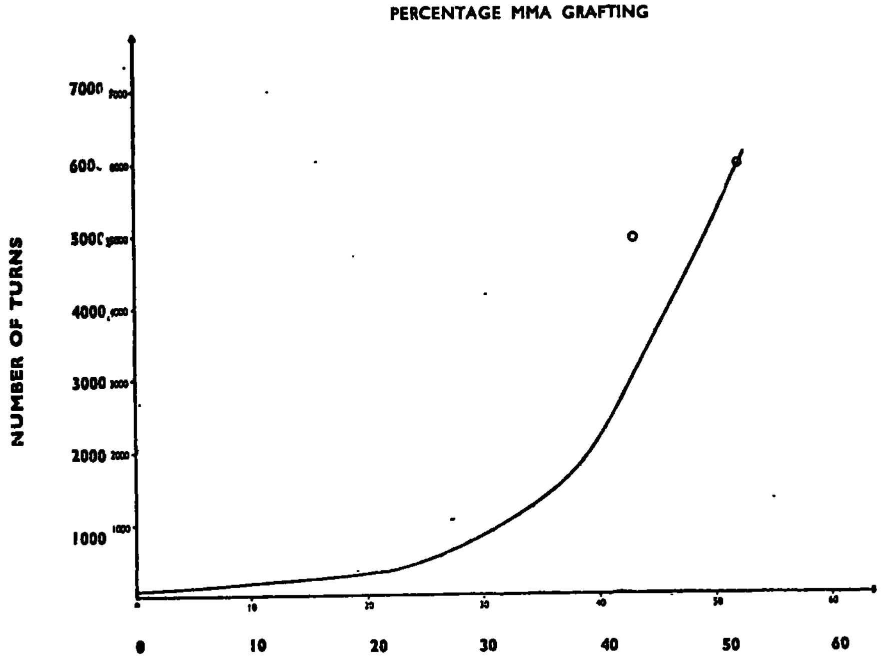

Fig. 2. Variations in rubfastness property with the % of grafting

of the highly grafted latex. It was found that 30-40% MMA graft copolymerized latex is most suitable as a binder because of its high resistance against abrasion and better adherence to the leather surface.

One disadvantage in the use of rubber latex as a binder is that it makes the leather surface somewhat tacky. This is mainly caused by the smaller particles in the field latex and can be avoided to a certain extent, by prevulcanizing the graft copolymerized NR latex using sulphur. Graft copolymerized and prevulcanized NR latex gives a smooth finish resembling the synthetic latices, but in addition it produces a high glossy finish. The formulation used for prevulcanizing methyl methacrylate graft polymerized latex is in parts by weight (wet) as follows :—

Grafted NR latex	286
20% potassium salt of coconut fatty acid solution	4
50% sulphur dispersion	1
50% zinc oxide dispersion	0.5
50% ZDC dispersion	1.2
50% Nonox EXN dispersion	2

The compounded latex was stirred and kept at 75°C for approximately 1 hr stirring at about 10 rpm. The prevulcanized latex was cooled and strained before use through fine gauze to remove any clots or particles that may be present.

Accelerated oven-ageing at 70°C for 72 hr of leathers finished using rubber which had been stabilized with the antioxidant Nonox EXN did not show any sign of oxidation. Leather finished with grafted field latex was also unaffected even after four months' exposure to direct sunlight.

CONCLUSIONS

These investigations revealed that the graft copolymerized natural rubber latex could be used as a substitute for imported synthetic binders and in this connection a patent has been filed relating to the use of modified rubber latex in leather finishes (Wickremasinghe *et al.*, 1972).

The annual requirement of binders for leather finishes is about 20,000 kg and this will cost the Corporation about Rs. 200,000. A saving of about one lakh of rupees in foreign exchange is expected by using this process. However the data collected so far regarding its ageing properties, scuff resistance etc., are insufficient to completely substitute imported synthetic binders. Therefore we recommend that the Ceylon Leather Products Corporation substitute only 50% of binders imported for finishing embossed and lining leather by grafted latex and this will save about Rs. 30,000 of valuable foreign exchange per year. The grafted latex necessary for use of the Corporation could be conveniently made at the Corporation itself.

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