

Use of Natural Rubber Latex in Paints

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Polymers in latex form have recently been introduced in water-thinned paints as film binders. The latices used in emulsion paints have been exclusively of the synthetic types. Initial experiments using natural rubber latex in such paints showed its serious disadvantages in hardness, stability, brushability and pigment-binding capacity. These properties were improved by grafting natural rubber latex with a monomer such as styrene or methylmethacrylate, vulcanisation using cumene hydroperoxide or by a combination of both methods. Emulsion paints made from stabilised field latex can be manufactured easily by these methods in natural rubber producing countries to displace distemper paints.

Emulsion paints were evolved as an improvement on earlier distempers and whitewashes, in which the water-soluble binder was replaced by water-insoluble binders such as latices or oily water-insoluble binders in the form of emulsions. Natural rubber latex is a tempting product for the water paint manufacturer. *British Patent No. 244 150 (1924)* covers the preparation of water-proof paint from latex by mixing with soluble caseinate and pigment; *British Patent No. 245 540 (1924)* describes the use of latex with any readily prepared commercial distemper.

Use of latex in water paints and distempers is beset with difficulties, the major one being the clogging of bristles during the application of distempers containing latex. Presumably the rubber latex is coagulated by the friction of the hair tips on the wall surface. A water paint which will brush out satisfactorily, wash down well and show very little discoloration on ageing was made as follows (STEVENS AND HEATON, 1933):

Glue solution	25	parts by wt
Casein solution	25	"
Latex	30	"
Lithopone	100	"

However, it was found almost impossible to clean a brush in which a latex mixture had

dried and this would be a serious drawback to manufacturers and users alike.

NOBLE (1953) suggested the following composition as suitable for latex paints:

	A	B
Rubber (as 60% latex)	100	100
Casein	8	5
Water	100	22
Pigment	70	40
Linseed oil	5	3

A difficulty arose with the latex mixture becoming coagulated on the brush because of the friction in brushing. The mixing of glue with casein, the protective agent, gave some improved results.

The post-war search in the United States for new outlets for synthetic rubbers led, in 1948, to styrene/butadiene latices being used as binders in paints. These latices had a higher styrene content and less odour than the G.R.S. type rubber; latex paints made from them were readily accepted and rapidly displaced traditional distempers. In recent years, the growth of synthetic latex usage in the house paints industry in the United States has mainly been in polyvinyl acetate rather than styrene/butadiene. In Europe, the latter has never been important since, from the beginning, polyvinyl acetate was the preferred available material and its technical superiority was generally admitted. About 1957, the first exterior water-based house paints were introduced. Most of them

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were based on acrylic type latices and they had outstanding colour retention on exterior exposure. MILES AND HARRISON (1967) have stated that emulsion paint production in Britain has had a growth rate of 13% per year since 1958, while the paint production has increased by 3% per year. The production of distemper however has continued to fall. The pigment volume concentration (p.v.c.) of typical, all-purpose emulsion paints increased from 25 to 30% in 1958 to 40% and above in 1965.

Natural rubber latex is not at present used for making emulsion paints and it would be a boom to natural rubber producing countries if this can be achieved.

The particle size of the emulsion media, i.e., latex in latex paints may have a profound effect on the rheological behaviour of the paints. According to BONDY (1962) the best particle size range of the emulsion media probably lies between 0.2 and 0.8 microns. The particle size of synthetic latices is usually fairly small being of the order of 0.07 microns and synthetic rubber latex manufacturers have therefore striven to produce materials of rather larger particle size than is normally found in synthetic rubber dispersions, for use in emulsion paints. The average particle sizes of synthetic latices used in emulsion paints ranges from 0.1 to 2 microns.

VAN DEN TEMPEL (1952), from electron microscope studies, found that the particle size of natural rubber field latex ranges from 0.04 to about 2 microns, the maximum in the size frequency curve occurring at approximately 0.6 microns. Less than 4% have diameters greater than 0.4 microns and this is roughly the fraction which can be observed through an ordinary optical microscope. This minority accounts for some 85% of the dispersed rubber.

SEKHAR (1960), using the soap titration method, has found the average particle size of field latex to range from 0.43 to 1.0 microns and that of concentrated centrifuged latex from 1.0 to 1.72 microns.

Hence from particle size considerations field latex appears to be more suitable than centrifuged latex for use in emulsion paints.

EXPERIMENTAL

Emulsion paints using natural latex were made as follows:

A dispersion of the pigment (titanium dioxide) and extender (kaolin or whiting) was made by milling them in an aqueous solution of dispersing (sodium hexameta phosphate) and thickening agent (carboxymethyl cellulose). A colloid mill or a high-speed disperser was used to prepare the dispersion. The formulation used (given in parts by weight) was:

TiO ₂ (Tioxide RC R-2)	—	125
Precipitated whiting	—	50
Carboxymethyl cellulose (2% solution)	—	100
Sodium hexametaphosphate (5% solution)	—	1.5
Nonox WSP	—	0.75

The latex was added to the pigment dispersion which was stirred adequately. The pigment volume concentration was 33% and 40%. The anti-oxidant used was Nonox WSP at a concentration of about 1 p.p.h.r.

The latices used were low ammonia (L.A.) field latex and high ammonia (H.A.) field latex prepared as follows:

- L.A. field latex*: Field latex treated with 0.35% ammonia and with diammonium hydrogen phosphate to precipitate and separate the magnesium and preserved with 0.3% sodium pentachlorophenate.
- H.A. field latex*: Field latex treated with 0.35% ammonia and with diammonium hydrogen phosphate to precipitate and separate the magnesium and the ammonia content brought up to 1%.

Unsaturated natural rubber is susceptible to oxidation, especially when exposed to sunlight. It is therefore unsuitable as an emulsion paint binder for outdoor use. Even in interior coatings, natural rubber latex cannot be used without modification, because of the risk of oxidation and poor brushability. Modifications attempted in the study were pre-vulcanisation, grafting and grafting with pre-vulcanisation. Each is discussed in turn.

Pre-Vulcanisation

Using sulphur. Pre-vulcanisation modifies the rubber hydrocarbon in natural rubber latex. The formulation used for pre-vulcanising L.A. field latex (given as dry weights) was: field latex 100, potassium hydroxide 0.3, sodium carboxymethyl cellulose 0.2, zinc oxide 1, zinc diethyldithiocarbamate 1, and sulphur 2. The last three were added as a 50% slurry. The compounded latex was stirred and kept at 70–80°C for 1½ hours. Emulsion paints made from this latex were easily brushable but had a yellowish colour with a tendency to chalk in three weeks after application.

Using tetramethylthiuram disulphide. Pre-vulcanised latex was made using the tetramethylthiuram disulphide (TMTD) vulcanisation system of latex as given in *N.R.P.R.A. Technical Bulletin No. 5*. Low ammonia field latex was heated at 70°C for three hours with the following (in parts by weight dry):

Field latex	100
Zinc oxide	1
TMTD	3
Thiourea	1
ZDC	1
Sodium carboxymethyl cellulose	0.2

Emulsion paints made from this latex were brushable but still had the defect of chalking a month after application.

Using cumene hydroperoxide. Since conventional vulcanisation systems did not yield satisfactory results, vulcanisation of natural field latex using tetraethylene pentamine (TEP) and cumene hydroperoxide (CHP) was investigated. BLOOMFIELD (1952) has suggested the use of 0.4 part of CHP and 0.4 part of TEP for 100 parts of 30% latex. SEKHAR (1962) has shown that field latex contains reduction activators at about 0.14 to 0.30% TEP equivalent of serum. Hence, the amount of TEP used by the authors was lower than the level suggested by Bloomfield, but they used a higher amount of CHP. The quantities used were 0.6 or 1 part of CHP and 0.25 part of TEP per 100 parts of H.A. field latex. The CHP was emulsified with coconut fatty acid and ammonia. One part by

weight of coconut fatty acid was mixed with 50 parts by weight of CHP and the mixture added with stirring to 149 parts by weight of 1% ammonia. TEP was added as a 10% solution.

The field latex, after adding CHP and TEP, was left at room temperature for at least 48 hours before use. Emulsion paints made from these latices were satisfactory as regards brushability but were not hard enough.

Hydroxylamine was also used as a reduction activator instead of TEP according to the following formulation (given in parts by weight):

H.A. field latex	100
20% potassium oleate	0.6
CHP	0.6
Hydroxylamine hydrochloride	0.2
0.25% Fe ⁺⁺⁺	5.0

A 50% hydroxylamine hydrochloride solution was made and neutralised with ammonia before addition. Pre-vulcanisation occurs at room temperature and the latex is ready for use after 48 hours. The Fe⁺⁺⁺ solution was prepared as follows (given in parts by weight):

Ferric sulphate	2
Sodium pyrophosphate	10
Water	100

Emulsion paints made from this latex were easily brushable, but were not hard enough.

Graft Polymerisation of NR Latex with Methyl Methacrylate or Styrene

Emulsion paints made from pre-vulcanised latex were rubbery and not as hard as those from synthetic latices. Styrene and methyl methacrylate (MMA), being important monomers used in making synthetic emulsion paints, were grafted with natural rubber to increase its hardness. BLOOMFIELD (1952) has shown that graft polymers with natural rubber in latex form can be prepared with either styrene or MMA using a polyamine-activated hydroperoxide. The method followed by the authors was that given by MUTHURAJAH (1964) for the preparation of MMA-grafted rubber latex from field latex; however, coconut oil fatty acid was used instead of oleic acid. The same method was also followed for preparation of styrene-grafted field latex with the modification that

TABLE 1. RESULTS OF TESTING IN WEATHEROMETER OF EMULSION PAINTS MADE FROM H.A. LATEX GRAFTED WITH MMA (p.v.c. 40%)

MMA (%)	Results of testing			
	Brushability	Film formation	Hardness	Tendency to chalk
0	poor	good	soft film, very rubbery	becomes sticky with time and rolls out on scrubbing, severe chalking
5	good	good	soft film	severe chalking
10	good	good	satisfactory hardness	severe chalking
15	good	good	satisfactory hardness	chalking
20	good	good	satisfactory hardness	satisfactory
25	good	good	satisfactory hardness	satisfactory
30	good	good	satisfactory hardness	satisfactory
35	good	good	hard	chalking

carboxymethyl cellulose at 0.02% on the latex was used as a stabiliser and TEP was added after the addition of the emulsified styrene and after the field latex had been heated to 55°C. This temperature was maintained, with occasional stirring, for about 6 hours. Emulsion paints made from the grafted latices were easily brushable but were somewhat hard.

Graft Polymerisation of NR Latex with Methyl Methacrylate or Styrene followed by Pre-Vulcanisation with Cumene Hydroperoxide

Even after grafting, there would be a considerable number of double bonds in the rubber molecule and they could have an adverse effect on emulsion paints made from such latices. Pre-vulcanisation of grafted latex with cumene hydroperoxide activated by TEP or by hydroxylamine hydrochloride should decrease the number of double bonds in the rubber molecule and hence should give improved weathering properties to such grafted and cumene hydroperoxide vulcanised latex.

RESULTS AND DISCUSSION

Emulsion paints made from grafted latices and those in which grafting was followed by peroxide vulcanisation were tested for seven days in a weatherometer. The results were:

1. Peroxide vulcanisation of the grafted latices gave improved hardness and weathering resistance;
2. As the MMA or styrene content increased, the brushability of the emulsion paint was better, the hardness of the emulsion paint increased and the pigment-binding capacity of the latex was reduced.

All the paint films showed yellowing and were not suitable in pure white shades. The hardness of the films improved with exposure. The pigment-binding capacity increased with reduction in pigment volume concentration.

The MMA content of the latices tested was 5, 10, 15, 20, 25, 30, 35 and 40% and the styrene content was 5, 10, 15, 20 and 25%.

MMA would be expected to be the preferred monomer for commercial use even though styrene is cheaper. This is because the MMA grafted latices are more easily prepared and they show much less yellowing in emulsion paints than the styrene-grafted latices. The results obtained by testing in a weatherometer of emulsion paints made (1) from H.A. latex grafted with MMA, and (2) from H.A. latex grafted with MMA and then vulcanised with cumene hydroperoxide, are given in *Tables 1*

TABLE 2. RESULTS OF TESTING IN WEATHEROMETER OF EMULSION PAINTS MADE FROM H.A. LATEX GRAFTED WITH MMA AND VULCANISED WITH CUMENE HYDROPEROXIDE (p.v.c. 40%)

MMA (%)	Results of testing			
	Brushability	Film formation	Hardness	Tendency to chalk
0	satisfactory	good	rubbery	severe chalking
5	satisfactory	good	rubbery but harder than control	chalking
10	satisfactory	good	satisfactory hardness	slight chalking
15	satisfactory	good	satisfactory hardness	satisfactory
20	satisfactory	good	satisfactory hardness	satisfactory
25	satisfactory	good	satisfactory hardness	chalking
30	satisfactory	good	hard	chalking

and 2 respectively. It will be seen that satisfactory emulsion paints are obtained with MMA contents of 20, 25 and 30% (Table 1) and with MMA contents of 15 and 20% (Table 2).

An emulsion paint made from H.A. field latex grafted with 15% MMA followed by pre-vulcanisation with cumene hydroperoxide has been applied on an interior wall and is showing satisfactory performance eight months after application.

A Ceylon patent (GANESHASUNDARAM AND NADARAJAH, 1967) has been obtained for the use of grafted, pre-vulcanised and grafted pre-vulcanised natural rubber latices in emulsion paints. The dry rubber content (d.r.c.) of the H.A. field latex could be maintained at a known level (35%), by using 60% centrifuged latex.

The paints having natural rubber field latex as the binder have fair washability within thirty days after application. However, their scrubability is not of the standard of synthetic emulsion paints. The use of a lower pigment volume concentration would improve the scrubability, but on the other hand, according to BONDY (1962), the yellowing and oxidative breakdown can be avoided or at least masked by the use of high pigment loadings. For natural rubber field latex we have found a p.v.c. of 40% to be satisfactory.

CONCLUSIONS

Emulsion paints made from grafted, peroxide-vulcanised (especially those from grafted and peroxide-vulcanised) latices increase in hardness with time. This may be explained by the fact that, together with stickiness, hardening is one of the principal changes which oxygen brings about in rubber. Hardening in the case of emulsion paints appears to be initiated by an active form of oxygen which reacts with the natural rubber under the influence of light.

The vulcanisation of field latex by 1 part CHP and 0.25 part TEP is the simplest way of modifying natural rubber latex for use as a binder in paints. At least 24 hours' interval between successive coats is necessary to allow the paint to harden. The replacement of about 10% of natural rubber latex by synthetic latices such as Wresimul 40 200* upgrades the paint in hardness and adhesion.

When the grafted latices were dried, the films had a tendency to crack when the MMA or styrene content was over 15%. This may be due to the non-uniform distribution of MMA or styrene within the rubber particles, resulting in a higher concentration of polymer at or near the surface. This would reduce the particle-to-particle adhesion at high styrene or MMA content of the grafted latices during drying,

*From Resinous Chemicals Ltd., Blaydon on Tyne, Durham, England

resulting in films which crack. ANDREWS AND TURNER (1960) have examined surfaces of torn films of graft polymer latices under electron microscope and have seen particulate regions of polymethyl methacrylate conspicuously on the surface of the particles. This explains the lower pigment-binding capacity of the latex at higher MMA or styrene content in the latex. But, an emulsion paint of 33% p.v.c., made from a grafted latex containing 40% MMA, was satisfactory in film formation.

Diammonium hydrogen phosphate, used to precipitate magnesium in the preparation of field latex, is, according to *N.R.P.R.A. Technical Information Sheet No. 93*, an anti-oxidant which protects vulcanised latex products against oxidation. Hence its use in slight excess would be beneficial. Rubbers treated with hydroxylamine show considerable resistance to sunlight and air degradation (RUBBER RESEARCH INSTITUTE OF MALAYA, 1967). Hence emulsion paints using latices with hydroxylamine as the reduction activator would be expected to have better ageing resistance. An anti-oxidant, Nonox EXN or Nonox WSL (1 p.p.h.r.) was added as a suspension or as an emulsion to the pigment during the preparation of the pigment dispersion. According to PHILPOTT (1969), in view of the low effectiveness of the anti-oxidants of the conventional radical chain breaking type, when used with unvulcanised rubber, an anti-oxidant such as thiourea may be a better anti-oxidant. A combination of thiourea at 0.5 p.p.h.r. and a conventional anti-oxidant Nonox EXN or Nonox WSL at 1 p.p.h.r. may be the best combination.

Fungicides must be added to natural rubber latex emulsion paints. Phenyl mercuric acetate or sodium pentachlorophenate can be added at 0.05% or at 0.6% respectively of the total weight of the paint. It is also necessary to add anti-foam agents to emulsion paints made from natural rubber latex.

The emulsion paints from the natural rubber latices described in this article are inferior in hardness and durability to emulsion paints from the synthetic latices. They would, however, be expected to displace distemper paints in the natural rubber producing countries.

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DISCUSSION

Chairman: Dr. J.-P. Poliniere

M. A.D.T. Gorton asked how brushability was determined and what caused destabilisation of the latex at the bristle tips. Mr. Nadarajah replied that brushability was not estimated quantitatively but by practical assessment, including how easily the brush could be washed after use and freedom from coagulation on the brush-tip. This coagulation was probably due to mechanical destabilisation and to latex particle-adhesion, agglomeration and coalescence; it was eliminated by grafting MMA or by pre-vulcanising with cumene hydroperoxide. The addition of soaps, as in certain types of latex concentrate, was not satisfactory for this purpose. Mr. T.D. Pendle commented that very high shear rates were experienced in brushing so that brushability required a high degree of mechanical stability. Whereas a latex concentrate with a large soap content was chemically rather than mechanically stable, a certain amount of soap was still used in preparing the M.S.T. graft to enhance brushability. He asked how a satisfactory film formation was obtained with a graft polymer latex containing 40% MMA, although cracking was reported for contents of more than 15% MMA. Mr. Nadarajah replied that 'total solids' films of 15% MMA cracked owing to their thickness, but when applied thinly as an emulsion paint, there was no cracking visible even at 40% MMA. Mr. P.S. Chin said that a latex obtained by the multi-stage grafting process had better filming properties than that obtained in a single stage. Mr. Nadarajah said although filming might be better after multi-stage grafting there might be no increase in hardness of the paint film.

Mr. H.J.M. Langshaw said it was interesting to see this subject reopened after thirty years when alkyds were emulsified in field latex and later in synthetic latex. He enquired how the formulation of the pigmentation was derived, for instance that containing titanium oxide and precipitated whiting, as the latter might cause difficulty with the base of natural latex. He asked if the hiding and covering powers of the paints had been tested. Mr. Nadarajah said the paint became more rubbery at the lower pigment volume concentrations. The sample exhibited was 35% p.v.c. Although the calcium ions in whiting might be expected to destabilise field latex, the results were satisfactory in the latex emulsion paint whose stability had been enhanced by grafting. Whiting was an inexpensive filler and recognised extender in emulsion paints; however, its covering power had not yet been tested.

Dr. G.F. Bloomfield suggested that acrylate grafts might have advantages in light ageing, but Mr. Nadarajah said these had not yet been tried. Dr. B. Saville considered improvement in light ageing (by finding non-volatile light stabilisers which would make the paint last longer) essential for acceptance where the cost of labour to apply was high. Mr. Gorton wondered if paints based on natural rubber latex could compete with the acrylate types of paint already available. Mr. Nadarajah agreed but indicated that the current opportunities were in a field intermediate between distempers and emulsion paints; however, further research and application of advances in emulsion technology—especially finding suitable light stabilisers—might improve the latex-based product to the level reached by synthetic latices with their twenty years' start. Mr. K.C. Sekar asked if creamed skim had been tried instead of field latex or centrifuged concentrate. Mr. Nadarajah replied that creamed skim had not yet been tried, but it was very viscous at 40% d.r.c. and would have to be diluted to 25% before grafting to get satisfactory results whereas field latex could be grafted at 35%. The small particle size of creamed skim might give a hardened product, but the larger amount of non-rubber substances—especially soluble substances—might adversely affect the washability and scrubability.