

INTERNAL PROTECTIVE COATINGS FOR LATEX CONTAINERS

INVESTIGATIONS ON INTERNAL PROTECTIVE COATINGS FOR
LATEX CONTAINERS AND THEIR VALUE IN MINIMISING
DISCOLOURATION IN PRESERVED LATEX

BY

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Introduction

In a previous publication (1) the present authors have discussed fully the causes of discolouration in preserved latex and have shown that the iron drum which is in common use as a latex-shipment vessel is in itself a pre-disposing factor to the discolouration of latex. Users do not however look with favour on the substitution of a non-metallic container for the steel drum, and since suitable alternative metallic containers are prohibitive in cost, there remains little alternative but to endeavour, by the internal application of some protective medium, to reduce to a minimum the objectionable effects of the iron drum on its contents.

Since discolouration is due to the formation of dark-coloured colloidal and amorphous sulphides of iron, a satisfactory drum-coating medium should prevent contact of the latex with the iron of the drum, and also if possible react with any sulphur bodies which may be liberated in the latex, to form sulphides which are either white in colour or so nearly white that when present in latex they are not detectable by the eye.

It is essential that the coating should not be so brittle as to crack or flake away from the metal when drums are roughly handled in transit. If flaking occurs, serious contamination of the latex may result. The requirement is a tough, elastic film which will adhere well to the metal and which will not be appreciably affected by long contact with ammoniated latex, except in so far as it may combine with sulphur bodies to produce a white product.

The present paper describes tests which have been made on a great variety of paint-like preparations some of which were proprietary and others which were compounded in the laboratory.

In testing the various preparations, the fact has been kept in mind that, in the majority of cases, the preparation must be applied to the inside of an already-assembled drum having at most two small apertures. This implies that preparations which

are normally slow to dry and harden do not commend themselves, because the drying time in the interior of a drum is necessarily longer than in freely-circulating air. Further, the only method of application available to most estates is that of pouring an excess of the preparation into the drum, rolling, turning end over end and finally running off the excess material. The construction of most drums does not lend itself to easy and complete drainage so that the only readily available method of application must be considered wasteful as well as troublesome. This fact suggests in turn that suitable materials should be such as are effective in a single application or coat. In all cases therefore tests have been confined deliberately to metal carrying one coat only of any given preparation.

Experimental

METHOD OF TESTING

The laboratory technique adopted for testing the suitability of the various media was empirical and was based largely upon the investigations which were made in connection with the earlier investigation (*loc. cit.*) into the causes of discolouration.

Strips of metal cut from an ordinary latex drum were given one coat of the material to be tested, by dipping and allowing to drain. After drying by exposure to free air for 24 hours at laboratory temperature, they were taken for test or if not reasonably dry they were recorded as probably unsuitable. In the course of all tests, unpainted strips were used as controls for purposes of comparison.

Two tests, which in practice were found to differ in severity, were applied to each material. These were:—

TEST (i)—THE SIMPLE IMMERSION AND STORAGE TEST and

TEST (ii)—TEST BY PARTIAL PUTREFACTION PRIOR TO AMMONIATION AND STORAGE

The details of each test follow:—

TEST (i)—THE SIMPLE IMMERSION AND STORAGE TEST

In this test coated strips and their uncoated controls were immersed to within one-half inch of their length in latex which had been ammoniated to approximately 1 per cent NH_3 while still in a fresh condition. They were then stored for a period of six weeks during which periodical observation of the degree of discolouration of the latex was made. The period of six weeks was chosen as being the approximate and reasonable period of time which might elapse between despatch from the estate and examination by the buyer at destination.

TEST (ii)—TEST BY PARTIAL PUTREFACTION PRIOR TO AMMONIATION AND STORAGE

This test is much more drastic than the simple immersion test, and under it many coating media, which appeared fairly satisfactory under the conditions of the first test, permitted the induction of considerable discolouration in the latex and accordingly came under suspicion. The technique consisted in immersing the coated and uncoated strips in fresh latex containing no preservative, and allowing the whole to stand for a period of four hours before adding ammonia as preservative. During this initial four-hour period prior to ammoniation some incipient putrefaction occurs in the latex and the products of this biological activity have a particularly severe action on iron. After having ammoniated the latex to approximately 1 per cent NH_3 , it was stored for six weeks in contact with the metal strip, colour observations being made as in Test (i).

In both tests, at the end of the storage period and after final colour observations had been made on the latex, the strips were removed, washed with water and the condition of the filming material appraised. Media which under both tests prevented latex discolouration and which in addition were present as a hard, continuous but not brittle film at the end of the storage period were adjudged satisfactory; where very slight discolouration occurred in the latex, the medium was classified as imperfect and where appreciable discolouration was apparent, as unsatisfactory. The unsatisfactory media showed in practically every case appreciable softening and/or loosening of the film at the end of the storage period.

PROPRIETARY MATERIALS TESTED

It was at first considered likely that among the proprietary brands of paints and protective solutions which were available in Malaya and which could be obtained from Europe some would be found which combined cheapness with efficiency, and an examination of a number of proprietary materials of different general types was made. In most cases the manufacturers were pre-informed of the requirements and supplied media which were expected to be satisfactory. The results of the examination of these materials are summarised in Table I.

The tests on the proprietary materials indicated that the only really satisfactory material was preparation No. 10 of which the base consisted of chlorinated rubber. In addition, preparation No. 9 containing chlorinated naphthalene showed promise, together with No. 24 which is in the main a derivative of rubber, and No. 13 which is a patented and rather expensive preparation

TABLE I

Key No. of paint	Type of base	Observations on drying rate	Condition of film after six weeks' storage of painted strip in latex	Suitability of paint as judged by degree of discolouration in Tests (i) and (ii)	General Remarks
1	Bituminous	Rather slow	—	Unsatisfactory	Unsuitable
2	"	Satisfactory	Continuous. Soft	"	"
3	"	"	" "	"	"
4	"	Rather slow	" "	"	"
5	"	" "	" "	"	"
6	"	Too slow	" "	Imperfect	Unsuitable because of slow drying
7	"	" "	" "	Unsatisfactory	Unsuitable
8	Pigment, in oil vehicle	Satisfactory	Softened. Fell away	Satisfactory	Unsuitable because film leaves metal
9	Chlorinated, Naphthalene	Satisfactory	Continuous. Hard	Imperfect	Fairly satisfactory
10	Chlorinated Rubber	Satisfactory	" "	Satisfactory	Suitable
11	Soluble bakelite	"	" Soft	Unsatisfactory	Unsuitable
12	"	"	" Fairly hard	"	"
13	"	"	Continuous. Hard	Imperfect	Fairly satisfactory
14	Not known	"	Softened. Fell away	Unsatisfactory	Unsuitable
15	" "	"	" "	"	"
16	" "	"	Continuous. Soft	Imperfect	Unsuitable. Film too soft
17	" "	"	" Fairly hard	Unsatisfactory	Unsuitable
18	" "	"	Continuous. Soft	"	"
19	" "	"	" "	Imperfect	Unsuitable. Film too soft
20	" "	"	Fell away	Unsatisfactory	Unsuitable
21	" "	"	Film breaking	"	"
22	Rubber derivative	"	Continuous. Hard	"	"
23	"	"	" Soft	"	"
24	"	"	" Hard	Imperfect	Fairly satisfactory
25	Not known	"	" Soft	Unsatisfactory	Unsuitable

of soluble bakelite. Chlorinated rubber and chlorinated naphthalenes are obtainable on the open market and this fact prompted further tests with media compounded in the laboratory from these bases.

LABORATORY-COMPOUNDED PREPARATIONS FROM PROPRIETARY BASES

Twelve different mixtures containing the chlorinated rubber "Pergut" with suitable solvents, softeners and plasticisers in different proportions, were subjected to the tests and all gave very satisfactory results. It was felt, however, that the process of compounding would be too difficult for the average estate and that the cost would be too great.

Twenty-three preparations containing chlorinated naphthalenes and mixtures of these bodies with bituminous substances as softeners, were prepared and tested. They were deemed to be unsuitable on grounds of difficulty of preparation and application. Many were in any case unsuitable because they permitted the induction of discolouration.

At this stage in the investigation the only reasonably satisfactory material which could be obtained in Malaya was the soluble bakelite preparation (No. 13) which is sold under the name of "Tropelite Black". This material has since been tested on a larger scale in large bulking tanks and trial drum shipments and, although not perfect, is nevertheless effective in minimising though not preventing discolouration. It is, however, too expensive for general adoption. The proprietary preparations Nos. 9, 10 and 24 were not and still are not available in Malaya.

The materials tested up to this stage had without exception been of the type which might protect iron from contact with latex but they were not compounded of substances which could readily react with any active sulphur bodies which might be produced in the latex. Since so little success had attended trials with the simple protective media, attention was turned to the production of a reactant filming medium. The aim was to produce a film containing a chemical substance which would react preferentially with latex-sulphur bodies to produce a white sulphide rather than the black sulphide of iron. Zinc oxide at once suggested itself as a suitable and cheap substance and laboratory tests were made with filming media containing zinc oxide as the essential principle.

PREPARATIONS CONTAINING ZINC OXIDE

(a) ZINC OXIDE IN AN OIL VEHICLE

Metal strips treated with paints in which zinc oxide was dispersed in an oil vehicle proved unsuitable. Latex discolouration did

not occur, but the film softened, fell away from the metal and contaminated the latex with its oily vehicle. The failure was judged to be due to an incorrect choice of vehicle.

(b) ZINC OXIDE IN RUBBER SOLUTIONS

Solutions of rubber in an organic solvent were used as a vehicle for zinc oxide. They gave zinc oxide films which adhered well to metal and which prevented latex discolouration. Rubber solutions are troublesome and expensive to prepare on estates and the obvious substitute was latex itself.

(c) ZINC OXIDE-LATEX FILMS

A number of zinc oxide-latex films were tested containing different proportions of zinc oxide and ammoniated latex. Very good results were obtained with these films. It remained to choose a mixture in which the proportion of zinc oxide was high enough to prevent latex discolouration but not so high that the deposited film of rubber and zinc oxide would be hard, lacking in adhesive power and likely to strip away from the metal. It was found that for best results the filming medium should contain approximately 20 per cent by weight of zinc oxide calculated on the weight of the ammoniated latex vehicles. In laboratory tests this filming medium gave consistently satisfactory results, and near the end of 1934 instructions for the use of this medium were first issued to an estate. The instructions are:—

"Take 2 lbs. of zinc oxide and mix to an extremely smooth paste with one quart of water. Mix this paste very thoroughly with one gallon of ammoniated latex containing 0.7 per cent ammonia. The mixture is now ready for use as a filming medium.

It is inadvisable to prepare more of the complete filming agent than will suffice for one day's supply of latex. A week's supply of the zinc oxide-water paste can, however, be prepared without danger. This should be thoroughly stirred before drawing the daily supply for admixture with the ammoniated latex vehicle. Before application, the filming mixture should be thoroughly stirred because the zinc oxide tends to settle out. Filming is carried out by pouring an excess of the mixture into a clean drum, rolling, and turning end over end, so as to film all internal surfaces. The excess filming agent is then drained out and the drum is exposed to the sun to dry the internal film. When the film is dry the drum is then ready for filling with ammoniated latex."

Where second-hand oil drums are used, it is important that drums which have been cleaned should be filmed within a few hours. Rust spots rapidly develop on the inside of wet, oil-free

drums. If rust spots are present, the applied film may be unsatisfactory because either the rust spots may not be completely covered or the film, if continuous, may not adhere firmly to the metal.

LARGE-SCALE LATEX SHIPMENT TRIALS WITH DRUMS FILMED WITH LATEX-ZINC OXIDE MEDIUM

Large-scale latex shipment trials of several thousand gallons in latex-zinc oxide filmed drums were made early in 1935 by Mr. J. S. Laird, the Manager of Jemima Estate. These shipments were made on the basis of the laboratory tests set out above, and the customary cautious but time-consuming intermediate stages of small-scale trial shipments were thereby eliminated. Our thanks are due to him for the confidence which he showed and which proved fortunately not to be misplaced. Mr. J. B. Crockett, the President of Heveatex Corporation, Melrose, Mass., U.S.A., who in the fact of being willing to accept and report to us fully on latex from such consignments, rendered an equally great service.

A number of large-scale consignments have demonstrated that when the latex-zinc oxide filming medium is carefully applied, latex may be expected to arrive at destination in a good white condition. The film itself adheres well to the metal and cases of film-stripping in transit are few. These trials have demonstrated adequately the effectiveness of the film against discolouration caused by the metal container.

The trials have also demonstrated that the film possesses one disadvantage in that it tends to reduce the stability of the latex. We are advised however that if the buyer is previously made aware of the fact that drums have been filmed, he can in nearly all cases correct this reduction in stability without serious difficulty.

Discussion

The work on latex drum-filming media is a natural corollary to the earlier investigations (1) on the causes of latex discolouration. The effectiveness of the latex-zinc oxide medium which was developed after many fruitless tests on proprietary protectives, provides in itself a confirmation of the correctness of the original postulate that latex discolouration is due to the formation of amorphous and colloidal sulphide of iron within the latex. The substitution of zinc for iron as the reactant metal should, if the postulate be correct, result in the formation of white and therefore to the eye undetectable sulphides. Such has proved to be the case.

Within the last few weeks a British Patent No. 434,214 by the Metallgesellschaft Aktiengesellschaft has become available to

us. This patent provides for the addition of free zinc oxide to the preserved latex itself in order to prevent discolouration. In our treatment of the problem such a procedure was considered undesirable and was purposely avoided. The chief reason was that users might object to the deliberate addition of free powders such as this to latex before shipment. In the latex-zinc oxide films described, the zinc oxide present is held in a rubber matrix and is not free to enter the body of the latex. Further, the product of its reaction with the sulphur bodies of the latex, namely zinc sulphide, must itself remain to a large extent bound in that matrix. It is considered that the latex-zinc oxide film has the effect of preventing discolouration while giving rise to the minimum of what might be termed contamination.

It has been observed that the latex-zinc oxide films tend to reduce stability. This might have been expected but it is difficult to envisage how it can be avoided. The reduction in stability is almost certainly due to the formation of traces of soluble ammonium zincate by the action of ammonia on the zinc oxide film. The traces of zinc salt thus brought into solution, would naturally tend to reduce stability.

It is pointed out that the latex-zinc oxide film has not been tested by us in shipment trials with centrifugally concentrated latex. Because the filming is known to reduce stability, it is possible that where the dry rubber content is of the order of 60 per cent and where the concentrate is not heavily stabilised but preserved solely with ammonia, the reduction in stability may have more serious effects than are found with preserved field latex.

Similar remarks would apply but probably to a lesser degree in the case of gum-creamed latex. Producers of centrifugal and gum-creamed latex are therefore advised to proceed with caution in the use of the latex-zinc oxide drum-film and to make small trial shipments before attempting bulk consignments. It is also the fact that high natural stability in preserved normal latex is considered essential by a few users, and producers of such latex are advised wherever possible to consult the user before commencing the practice of filming with the latex-zinc oxide medium.

Summary

Tests on various drum-filming media as preventives of latex discolouration are described.

A simple filming medium effective against discolouration and compounded from latex and zinc oxide has been developed. Its possible disadvantage on the grounds of reduction of stability is discussed.

Literature cited

- (1) Rhodes, Edgar and Sekar, K.C., *J.R.R.I.M.* **5** (1934) 176

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