THE CAUSES OF DISCOLOURATION IN PRESERVED LATEX

BY

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Introduction

In recent years numerous processes have been developed for the application of latex to new manufactures. In many of these processes, the production of a satisfactory article is very largely dependent upon the colour of the preserved latex available; preserved latex of which the colour at the time of delivery to the user, is other than a good white, presents very serious difficulty in processing, and often yields an unsatisfactory product. The number of processes in which a good white latex is a matter of vital importance is increasing rapidly, and it is therefore not surprising that buyers have very rapidly become more discriminating in their choice of sources of supply, and more exacting in their requirements. So much importance is now attached to the characteristic of colour, that those suppliers who have been fortunate in establishing a reputation in European and American markets for the production of a latex which reaches destination in a good white condition, have earned for themselves an assured market, while many of those whose products were not until recently made the subject of complaint, have either lost or are in some danger of losing their markets. Estates wishing to enter the latex market have been called upon by buyers to ship trial consignments as a preliminary to the making of contracts and, in some of these cases, contracts have not been obtained, chiefly because the sample consignments of latex were of unsatisfactory colour on arrival at destination.

The nature of the buyer's complaint is that the latex on arrival at destination, often contains a considerable amount of a blue-grey sludge and that, apart from the presence of this undesirable material, the body of the latex retains a grey or blue-grey colour even after gravitational separation of the sludge. It is very frequently the case that when complaints are made against colour, one or other of certain complaints such as low stability, presence of an undue amount of coagulated rubber, and putrefactive odour, are also associated as rider objections. Complaints of this nature have occasioned some surprise to producers whose latex is undoubtedly of good colour at the time of packing in Malaya, but there is no gainsaying the fact that some latices do develop a very undesirable colour even in the comparatively short period of storage which is represented by the time taken for transport between Malaya and destination.

It has been shown by De Vries and collaborators, (1) and (2). that when latex is treated with ammonia, a precipitate is produced which contains insoluble phosphates together with a certain amount of rubber; that the precipitate is at first slightly yellow and that on long standing the precipitate tends to darken, when iron and hydrogen sulphide become detectable in it. The presence of iron in the deposit found in latex shipped in kerosene tins, has also been recorded, (3), but in the published literature there appears to be no reference to the discolouration which may take place in the body of the latex or to the causes of such discolouration. In view of the importance which now attaches to this characteristic, and in view of the fact that, unless users can obtain supplies of good white latex, present and future developments in the latex industry may be seriously hampered, it was considered desirable to attempt to discover the factors responsible for the development of the defect and to indicate if possible suitable measures against it.

Experimental

(a) EXPERIMENTS MADE WITH THE OBJECT OF DETERMINING THE ROLE, IF ANY, OF LATEX ENZYMES IN DISCOLOURATION

Various authors have noted the presence in latex of oxidising enzymes which cause the darkening of a coagulum through the colour stages of pink, and violet, to blue-black and it is a common estate practice to inhibit the action of these enzymes by the addition of sodium bisulphite to latex in the preparation of pale crepe. Eaton (4) and Morgan (5) have observed that by the addition of certain common phenolic bodies to a latex not normally prone to give a discoloured coagulum, a dark coloured rubber is obtained and De Jong (6) indicated that the addition of tyrosine to certain latices apparently containing the enzyme tyrosinase, resulted in a rubber of dark colour. De Vries (7) has noted the fact that during and after the wintering period, the tendency of latex to give a discoloured rubber, is more pronounced. Certain large buyers of latex have recently expressed the opinion that the tendency towards discolouration in the latex from various shipments throughout a year, appears to be to some extent seasonal. These facts taken together suggested the possibility that the tendency of preserved latex as distinct from rubber itself, to discolouration, might also be an enzymic phenomenon and a number of experiments were made to test this point.

(i) *Addition of accessory substances to preserved latex*

Good white latex, collected under normal estate conditions but preserved in glass vessels was treated with small amounts of a range of phenolic substances and stored for three weeks in order to discover whether the discolouration phenomena could be imitated and if

so by what type of accessory body. The substances employed were hydroquinone, orcin, resorcin, quinone, anthraquinone, β napthol α naphthol, phloroglucinol, metol, pyrogallol, amydol, tannic acid and gallic acid. With most of these materials a discolouration of the latex was obtained but this was either :—

(a) A surface oxidation in which the shade of colour obtained, was not the same as is observed in a naturally discoloured latex, and in which there was a gradient of colour intensity from the surface of the latex downwards, the lower layers being lightest in colour; in a naturally discoloured latex, the surface cream layers are almost always pure white in colour.

or (b) A uniform colour throughout the body of the latex, but of a shade different from that observed in a naturally discoloured latex.

It was concluded from these experiments that the simple addition of phenolic bodies to preserved latex does not reproduce the normal latex discolouration, by action as accessory substances to the enzymes normally present. In experiments described later in this paper, tyrosine was also added to latex as a specific accessory body for the enzyme tyrosinase, but the colour obtained was again of incorrect shade.

(ii) *Addition of enzyme activators and inhibitors*

Samples of latex collected and bulked under normal estate conditions and then preserved in glass vessels, were obtained from an estate whose latex shipments had been made the subject of complaint. When taken for experiment, the latex was of good colour. Ash analysis revealed the presence of an abnormal quantity of iron, but no importance was at the time attached to this fact. From this latex a series of tubes was set up for observation after the addition of traces of the various substances which follow :—

Substances unlikely to assist enzyme activity and which might retard it	Substances likely to assist enzymic activity when added in traces
Sodium hypochlorite	Ferric chloride
Bleaching powder	Ferrous sulphate
Alcohol	Hydrogen peroxide
Sodium bisulphite	Sodium peroxide
	Ammonium persulphate
	Calcium chloride
	Manganese chloride
	Potassium cyanide
	Tyrosine

From these experiments, which were repeated *in toto* on samples drawn from the bulked latex from each of a number of different days' crops, certain general conclusions became possible during an observation period of three weeks.

   (i) The control latex assumed slight discolouration.

   (ii) The substances added for the purpose of retarding enzyme activity did not yield a latex showing observable differences from the control latex.

   (iii) The tubes containing salts of iron, invariably showed an increase in discolouration over control and the type of discolouration was typical of that encountered in commercial latex.

   (iv) Traces of hydrogen peroxide, potassium cyanide, sodium peroxide, and ammonium persulphate produced no increase in discolouration and the tendency was rather to reduce it.

   (v) Calcium and manganese chlorides produced no observable effect on colour.

Of these conclusions the third and fourth were by far the most striking and prompted further experiments.

Working with similar samples drawn from bulked latex from the same source, several series of tubes were set up against controls. These were arranged

   (a) To test the effects of iron salts, hydrogen peroxide and potassium cyanide when applied singly. Hydrogen peroxide and potassium cyanide were added in various amounts ranging from traces, to amounts at which they would be expected to function as enzyme paralysers rather than as activators.

   (b) To test the combined effects of iron salts and hydrogen peroxide and potassium cyanide. The peroxide and cyanide were applied at various concentrations as under (a).

Observations were made over a period of two weeks and it became apparent that

   (i) Iron salts when applied alone, produced an increase in discolouration over the controls, which themselves showed noticeable discolouration.

   (ii) Hydrogen peroxide and potassium cyanide applied alone, showed in no case an increase of discolouration; with increase in concentration of added reagent, the colour was progressively whiter than the control and at the higher concentrations the colour was a good white.

   (iii) Hydrogen peroxide and potassium cyanide, when applied together with iron salts, in no case increased the tendency of the iron salts to produce discolouration, but tended to prevent it. At the higher concentrations of peroxide and cyanide, the degree of discolouration of the latex was less than was obtained with iron

salts alone, and was in most cases of the same order as that in the control latex.

The general indications at this stage were that, if the discolouration phenomenon were enzymic, the action must be fairly specifically activated by iron salts, since calcium and manganese salts were ineffective. Hydrogen peroxide, which would be expected to assist an enzymic oxidation process and increase discolouration, when applied in traces to latex, whether activated with iron or not, actually had the reverse effect. In view of the inconclusiveness of the evidence, further information was sought in an approach from a somewhat different angle.

In one method of estimation of tyrosinase activity, the dark coloured substance (melanin) formed, is oxidized by potassium permanganate to a colourless body and, if the discolouration of latex were due to an enzyme activity allied to that of tryosinase, then it should be possible to discharge the blue-grey colour of an *already discoloured latex,* by the action of oxidizing agents. Samples of badly discoloured latex which had been returned by an American buyer, were treated with potassium permanganate and the blue-grey colour was discharged; at the same time however brown manganese salts were precipitated. When treated as an alternative with 1 per cent. by volume of hydrogen peroxide (20 volumes) the colour was discharged immediately to a good white with a slight golden tinge. On standing for 24 hours, a brown precipitate settled out leaving a good white supernatant latex, (see Plate 2). Sodium peroxide and ammonium persulphate behaved similarly, though excess of the latter reagent tended to cause clotting. These observations, although quite indirect, could not be disregarded, since they did not detract from the circumstantial evidence for an enzymic interpretation of the problem. It was obviously desirable to obtain, if possible, evidence which would be more direct by making comparative discolouration experiments on latices of vigorous and less vigorous enzyme activities collected and preserved under standardised conditions.

By the courtesy of the manager of an estate in Selangor it was possible to obtain samples of latex which were ideal for the purpose. In a small area of mixed clones on this estate, certain members yield a latex which is of very vigorous oxidising enzyme activity, others a latex of lesser activity, and others a latex of practically no activity, as judged by the rapidity with which a coagulum obtained by alcohol coagulation, discolours through the stages of pink and violet to a final black; coagula from the more active samples begin to discolour within a few minutes of coagulation while those from the least active latex retain a good colour even after twenty four hours. It was possible therefore to collect latex of very different enzymic activity from trees on the same soil site, and growing within a few yards of each other. Latex was collected separately from

twelve selected trees, ammoniated in each case at the tree, and preserved in closed glass vessels, so that possible adventitious contamination was reduced to the practicable minimum. The enzymic activity of each latex was tested by alcohol coagulation on a small sample, with subsequent observation of the rapidity of appearance of discolouration on the coagulum. By this means the latices were divided into two widely different groups, one of which showed very vigorous enzyme activity and the other of which showed virtually no activity. Within two hours of collection, seven series of twelve tubes were set up. Each series contained a sample from each of the twelve selected latices. The various series covered the following treatments :—

(1) Preserved latex. Control.
(2)   „   „ with a trace of added ferric chloride.
(3)   „   „ with excess of added tyrosine.
(4)   „   „ with traces of added ferric chloride and tyrosine.
(5)   „   „ with a trace of added calcium chloride and excess tyrosine.
(6)   „   „ with a trace of hydrogen peroxide.
(7)   „   „ with excess of hydrogen peroxide.

The seven series of tubes were set aside for six weeks to give ample time for discolouration and at the end of this time the following observations became possible :—

(i) The twelve control tubes covering the simple preserved latex from enzymically active and inactive trees, were all of uniformly good white colour; no observable discolouration had occurred in any tube.

(ii) Every tube in both of the series containing added iron, showed some discolouration and the type of discolouration was typical of that shown by commercial latex.

(iii) In the two series containing excess of free tyrosine, a discolouration was observed but this was in no way similar to that found in commercial latex.

(iv) The two series treated with hydrogen peroxide exhibited uniformly good white latices identical with the controls.

(v) When, in the two series in which a true discolouration had been induced by the addition of ferric chloride, marks were given for colour intensity in each tube, the total number of marks awarded to the members of the active group was greater than that awarded to the inactive group. The marks awarded to individual members, could not however be correlated with their observed initial enzyme activities since three of the six members of the inactive group were each awarded as many marks as the lowest marked member of the active group, and two of the six members of the active group obtained no more marks than the highest marked member

of the inactive group. The addition of iron salts did not therefore in its induction of discolouration, reproduce the well marked differences which existed between the enzymic activity of each member of the active group compared with that of each member of the inactive group.

From this experiment the conclusion seemed inescapable that discolouration is not a simple function of enzyme activity; no control tube showed any discolouration and, since the controls included members which were already very active and therefore in no need of activation, these latices should clearly have been expected to show discolouration. The irregularity of the induction of colour by added iron salts produced no convincing evidence in favour of an enzymic explanation.

Before proceeding with further tests on enzymically active and inactive latices, experiments were made with commercial preserved latex stored in glass and in iron vessels, in order to discover whether the effect of iron salts added in solution, could be reproduced merely by contact with metallic iron. Excessive discolouration was repeatedly obtained in latex stored in iron tubes, when compared with controls stored in glass. Similarly by introducing a strip of drum metal into a glass tube containing latex, excessive discolouration over control, was usually observed after an interval of two to three weeks. Commercial latices from various sources showed however divergent rates of response to iron whether added as salts of iron or as the metal; some responded rapidly and showed appreciable discolouration in less than a week, while others reacted very slowly and showed but slight discolouration after a month's storage in contact with iron. No explanation of this fact presented itself at the time.

At this stage a further set of latex samples was obtained from the same twelve enzymically active and inactive trees mentioned earlier, and experiments were made to test whether or not discolouration was possible in the absence or in presence of metallic iron after having destroyed the enzymes by heat. Where heat treatment was applied, a test tube containing the ammoniated latex was immersed in an oil bath heated to a temperature of 180°C., so that the temperature of the latex should rise quickly to 85-90°C. The temperature of the latex was maintained in this zone for 15 minutes. At intervals a little ammonia was added to guard against coagulation. Four complete series of twelve tubes were prepared as under for observation :—

    (1) Preserved latex. Control. Unheated. No iron.

    (2)   „   „   Control. Heated. No iron.

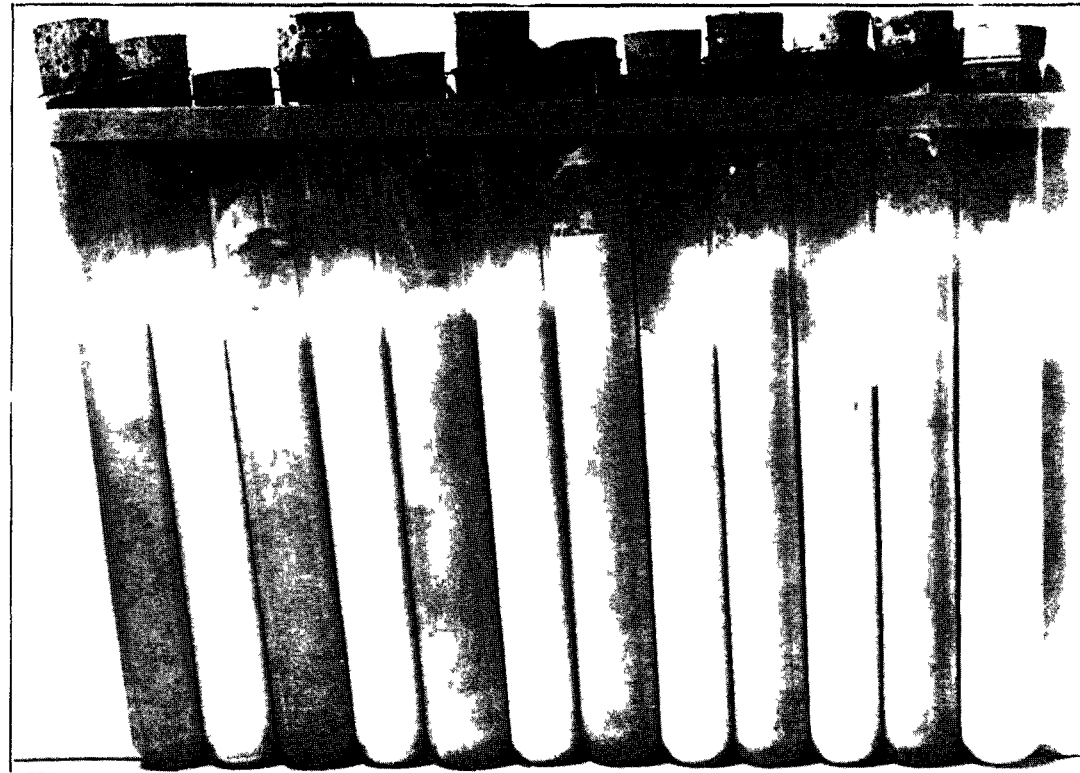   (3)   „   „   Unheated, with a strip of drum metal in each tube.

PLATE 1

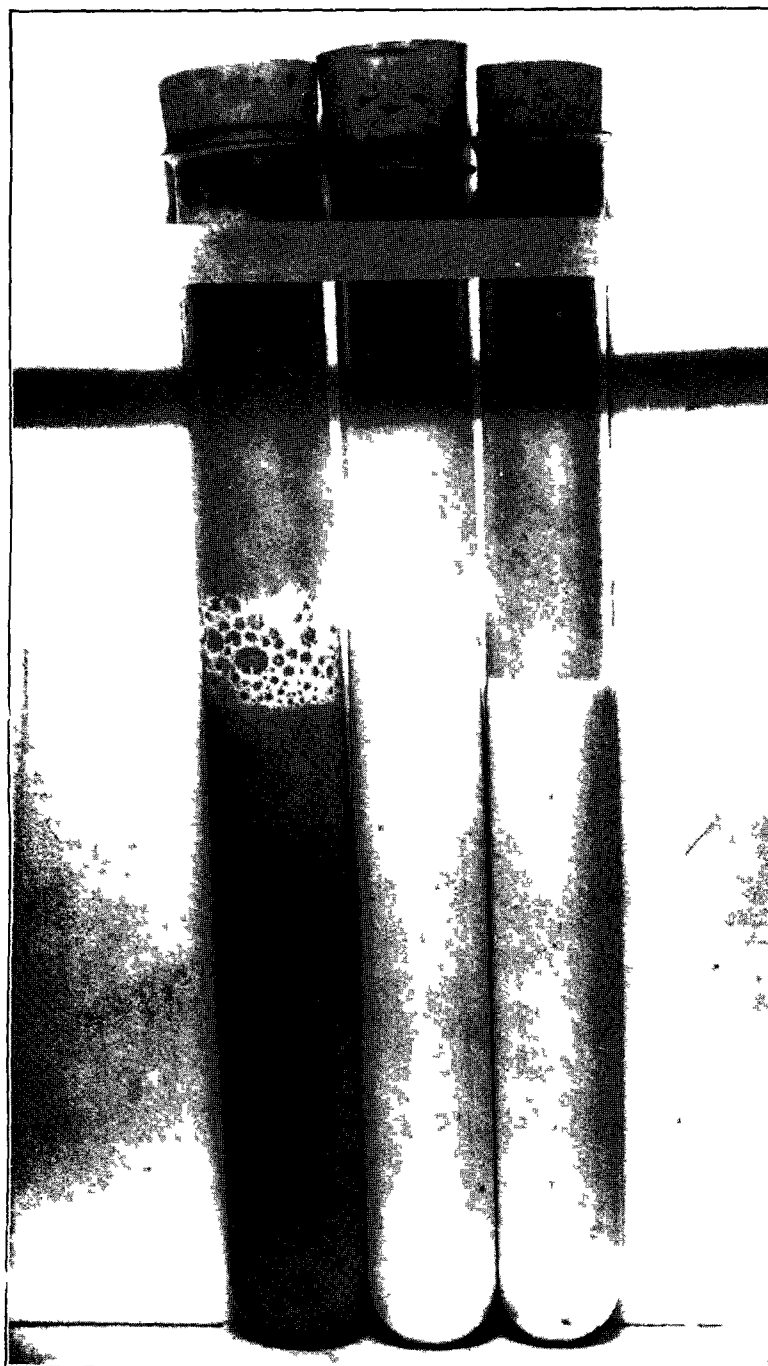*The induction of discolouration by iron*
For explanation see text

PLATE 2

Restoration of good colour to a discoloured latex

Left to right :—Discoloured latex, the effect of hydrogen peroxide,
and the effect of potassium cyanide

(4) Preserved latex. Heated and containing a strip of drum metal in each tube, the metal having been introduced after cooling the latex.

On these four series of tubes the following observations were made :—

(a) The two complete series of control tubes of unheated and heated latex still retained a good white colour after six weeks' storage. This confirmed the observation made in the previous similar experiment.

(b) Each member of the two complete series of tubes heated and unheated, but kept in presence of metallic iron, showed serious discolouration. The intensity of colour in the series of unheated tubes could not be correlated with enzymic activity.

(c) Of the two series of tubes containing iron, each member of the heated series *discoloured much more rapidly* than the corresponding unheated tube.

Plate 1 shows six pairs of tubes from this experiment which are typical of the differences exhibited by unheated control tubes after six weeks' storage and the corresponding tubes of unheated latex containing metallic iron. On the extreme left of the plate is a tube containing iron; its immediate neighbour is its own control without iron. Each succeeding pair represents a different latex. The pair on the extreme left and the pair on the extreme right are from enzymically inactive latices and the remaining four pairs are from enzymically active latices.

The fact that, after a heat treatment sufficient to destroy the enzymes, the rate of response to iron was actually increased, disposed finally of the possibility that discolouration might be due to enzyme activity. The exploration made, in testing this point, had however provided clear evidence that one of the causative factors is the presence of iron and that the effect of heat on latex is to increase its rate of response to discolouration by iron. A means of restoring a good colour to an already discoloured latex had also been found in the use of hydrogen peroxide and other oxidising agents and there was strong preliminary evidence that these bodies, when added to a latex of good colour, would delay the induction of discolouration by iron. Evidence was still required which would indicate the nature of the factor or factors complementary to iron and which with it result in discolouration.

(b) EXPERIMENTS WITH POTASSIUM CYANIDE AND HYDROGEN PEROXIDE AS PREVENTIVES OF DISCOLOURATON

The effect of potassium cyanide, in the earlier experiments with good white latex, had been similar to that of hydrogen peroxide in retarding the onset of discolouration, and it was now found that, like

hydrogen peroxide, it was able to restore a good colour to an already badly discoloured latex (See Plate 2). Its effect was not however instantaneous as in the case of hydrogen peroxide, but an amount of potassium cyanide equal to 0.075 per cent. of the weight of latex restored a good colour in a few minutes. Storage experiments, with discolouration-susceptible latex in sealed kerosene tins, indicated that a smaller amount, equal to 0.025 per cent. of potassium cyanide by weight, was sufficient to suspend the onset of discolouration for three weeks during which period an appreciable colour had developed in the control latex; in storage periods of two months however, an appreciable discolouration did develop in cyanide treated latex, but the colour was less marked than in the controls. In similar storage experiments with 1 per cent. by volume of hydrogen peroxide (20 volumes) similar results were obtained. Storage in presence of 0.075 per cent. potassium cyanide was effective for approximately five weeks but appreciable discolouration had developed in ten weeks; the discolouration was however less severe than in controls of the same latex.

In all cases in which discolouration had occurred on storage, either in the absence of hydrogen peroxide and potassium cyanide, or, after very long storage in their presence, a further treatment with either reagent restored a good colour.

In numerous experiments, where discolouration had been induced by the addition of soluble iron salts, or by the introduction of drum metal, the two reagents were invariably effective in discharging the colour.

(c) EXPERIMENTS TO DISCOVER THE FACTOR OR FACTORS COMPLEMENTARY TO IRON

Samples of the sludge, which is always found in naturally discoloured latices, were always found to yield hydrogen sulphide on treatment with mineral acid and the acidification was sufficient to discharge their dark colour. Iron was invariably present in the sludge, and the indication therefore was, that, in so far as concerned the colour of the sludge, as distinct from the discolouration which may be present throughout the body of the latex, the dark colour present is due to the formation of sulphides of iron and the factor complementary to iron would therefore be sulphur bodies.

It was at first considered somewhat unlikely that the discolouration which occurs in the body of the latex and which persists even through long settling periods, could also be attributed to sulphide formation, but experiments were made with fresh latex in order to discover whether, under conditions specially favourable to the formation of sulphides, discolouration as well as sludge deposition would be encouraged.

(i) *Experiments on latex partially putrefied in absence of iron*

Very fresh latex was obtained at the Institute at 9.30 a.m. and, after ammoniation of a control sample, the remainder was placed in a glass vessel and three further samples were drawn from it for ammoniation at intervals of approximately two hours, in order to follow progressively the effects of natural putrefaction; as bacterial putrefaction proceeds, hydrogen sulphide is produced and after ammoniation the readiness of the latex to produce sulphides in presence of iron, should be increased. As each sample was ammoniated, a strip of drum metal was inserted into the tube and the whole series was left for one month for observation. At the end of this time it became clear that latex which had been allowed to approach the stage of clotting in the absence of iron, before ammoniation and subsequent storage in presence of iron, showed appreciable discolouration and appreciable precipitation of dark coloured solids, while control latex, also stored in presence of iron, but ammoniated while very fresh. was yet in a good white condition. The observations indicated also that the discolouration in the body of the latex and the deposition of the dark coloured deposit proceeded simultaneously; in no case was a dark coloured deposit observed beneath a good white supernatant latex; rather was discolouration visible in the body of the latex as soon as, or before appreciable deposition of solids became apparent. Repetition of the whole experiment, confirmed these observations.

Commercial preserved latex which had been drawn from an estate bulk and stored in a glass vessel for a week before being taken for experiment, was placed in a tube with a strip of drum metal; a further sample of the same latex was partially de-ammoniated and set aside in air until putrefaction commenced, when it was re-ammoniated and again placed in a tube with a strip of drum metal. The partially putrefied re-ammoniated sample, discoloured most severely. Discolouration of the latex and deposition of dark solids proceeded simultaneously.

Fresh latex was placed in a collodion sac in a vessel of distilled water, and allowed to remain for seventeen hours during which time spontaneous coagulation proceeded within the sac. The clear unconcentrated dialysate from this latex, when ammoniated and treated with a trace of ferric chloride, gave a distinct blue-black colour in two hours, but no deposit was obtained.

The inference was drawn that deposition of dark sludge and discolouration in the body of the latex, were in some way connected.

(ii) *Experiments on latex partially putrefied in presence of iron*

In the previous putrefaction experiments the latex was not allow-ed to come into contact with iron, until the acids developed during

putrefaction, had been neutralized with ammonia. It was now sought to test the effect of putrefaction in presence of iron before ammoniation; in these experiments the acids developed, which would consist in the main of lactic acid, were therefore allowed to attack the iron before ammoniation, so that sulphur bodies and soluble iron would both be available in the latex at the moment of ammoniation.

The latex taken for these experiments was chosen not for its reactivity to iron, but for its peculiar resistance; normal preserved latex from this source, when in contact with iron for periods up to three months, shows little sign of discolouration or sludge deposition. Fresh latex, placed in a shallow dish containing strips of drum metal and allowed to putrefy, showed a blue discolouration in thin surface films immediately above the metal strips after four hours, that is when putrefaction, as judged by odour, was well advanced. Ammoniation at this stage gave an immediate blue-black discoloura- tion, but deposition of solids was not apparent for some hours. The ammonia treated latex was placed in a tube with a strip of drum metal and, in three days, developed an extremely bad discolouration and a heavy deposition of solids. Hydrogen peroxide and potassium cyanide discharged the dark colour of the latex and of the deposit.

In a further experiment with latex from the same source, an attempt was made to test progressively the effect of putrefaction in presence of iron, before full ammoniation and storage in presence of iron. A control sample of the latex was fully ammoniated when fresh from the field, and placed in a tube in presence of drum metal. In addition, fresh latex, and samples containing 0.05, 0.10 and 0.20 per cent. ammonia respectively, were exposed in presence of iron for 20 hours. At the end of this period, the fresh latex was badly clotted, putrefactive odours were very pronounced, and surface dis- colouration was visible. After sieving to remove clots and lump, the latex was ammoniated, when a distinct and typical *discolouration became apparent immediately*. The discoloured ammoniated latex was placed in a tube with drum metal and set aside for observation. The latex to which 0.05 per cent. of ammonia had been added before exposure, had a decided putrefactive odour after 20 hours, but severe clotting, such as had occurred in the fresh latex, was absent. Am- moniation, before storage in presence of drum metal, again revealed an immediate discolouration which was less pronounced than in the case of the exposed fresh latex. The latex containing 0.1 per cent. ammonia, had lost its ammoniacal odour during the exposure period, but putrefactive odours were not pronounced. On ammoniation a very faint discolouration appeared immediately. Where 0.2 per cent. ammonia had been added, the exposure period of 20 hours produced no putrefactive odour. On full ammoniation no immediate dis- colouration was apparent. The various tubes, now containing 0.5 per cent. ammonia and strips of metal, were kept under observation
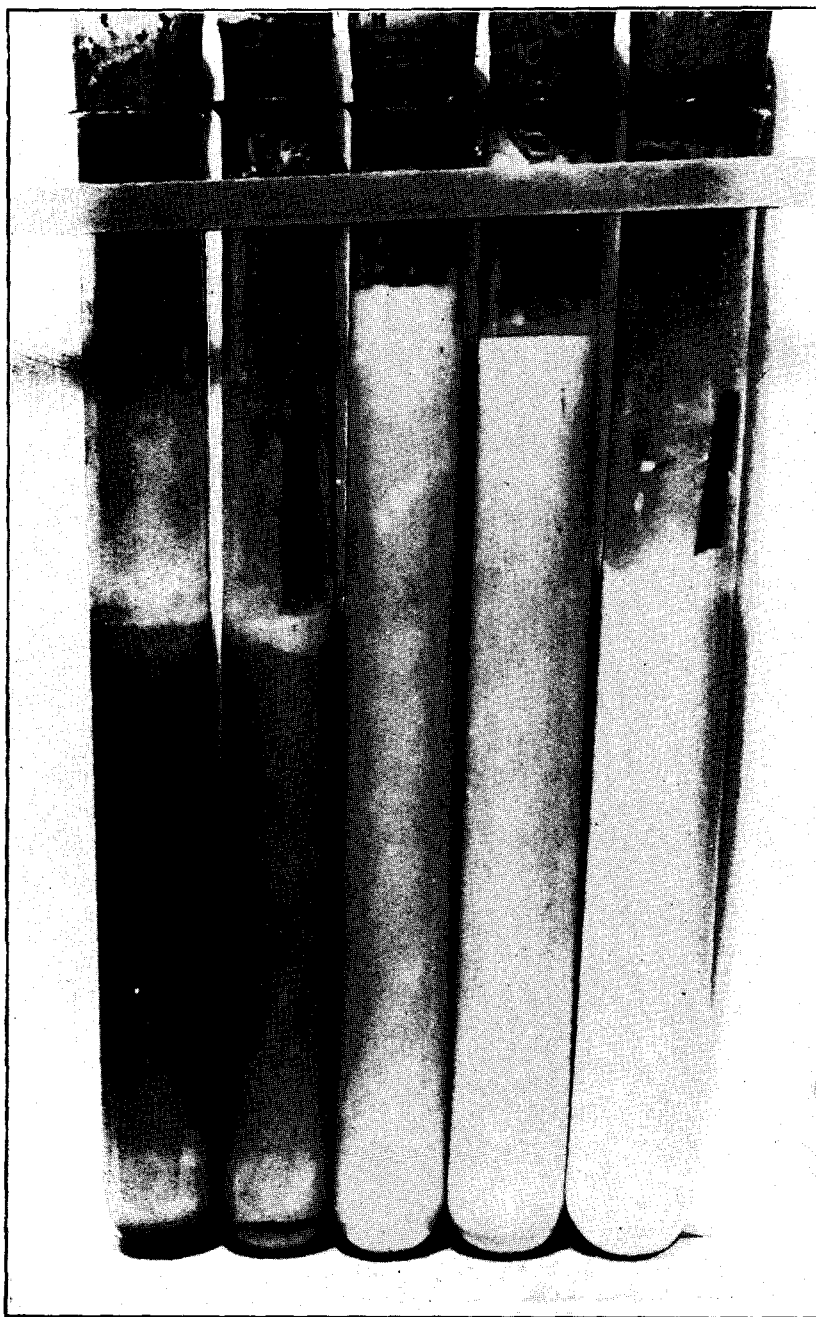
PLATE 3

*The effect of partial putrefaction in presence of iron
before ammoniation*

For explanation see text

for a week and at the end of this time discolouration and dark solid deposits were apparent in every tube save the control; Plate 3 shows the variation in the discolouration. From left to right the tubes are

1. Fresh latex severely putrefied before final ammoniation.
2. Latex containing 0.05 per cent. ammonia at the time of exposure. Putrefaction less severe before final ammoniation.
3. Latex containing 0.1 per cent. ammonia at the time of exposure. Putrefaction before final ammoniation less severe than in 2.
4 Latex containing 0.2 per cent. ammonia at the time of exposure. Putrefaction before ammoniation less severe than in 3.
5. Control latex ammoniated immediately and not exposed for putrefaction.

It is seen from the illustration that, while the control latex retained an exceedingly good colour. putrefaction in presence of iron initiated very serious discolouration.

The experiment also indicated that, even with a latex which is normally very resistant indeed to iron, there are conditions under which discolouration can be produced at the very moment of ammoniation. By causing the latex itself to provide a sufficiency of soluble iron and of hydrogen sulphide before ammoniation, these conditions are realised and discolouration is then apparent before deposition of dark solids commences. The inference was drawn that latex discolouration is probably a preliminary to deposition of solids and that the two manifestations are, in all probability, successive stages of the single process of sulphide formation.

In further experiments, evidence was obtained that, while the effect of heating a freshly preserved latex in presence of iron is generally to increase the rate of discolouration, the effect of heating a latex, which before ammoniation has been subjected to partial putrefaction in presence of iron. is still further to increase the rate of discolouration. In these experiments also, discolouration was a preliminary to deposition of solids and the conviction was thereby strengthened that the appearance of discolouration in latex merely marks the beginning of a sulphide formation in which some, but not all the sulphide is later deposited.

A badly discoloured commercial latex was separated from its heavy sludge and set up for creaming with gum tragacanth. The serum obtained was of a deep blue-black colour; the colour was discharged by hydrochloric acid and the acid solution responded to tests for iron. Further if the discolouration is due essentially to the presence of traces of finely dispersed or colloidal iron sulphide, exposure of the blue-black serum to air should discharge the discolouration in a few hours, and hydrogen peroxide should dispel it instantly. The serum was separated. A portion was exposed to air

and another portion was treated with hydrogen peroxide. In both cases the colour was discharged; in the first case overnight and in the second case instantly.

It remained to demonstrate that discolouration and sludge deposition could be induced in latex by purely artificial means

(iii) *Artificial discolouration of latex*

It is well known that, if very dilute solutions of iron salts are treated with ammonium sulphide or with hydrogen sulphide in alkaline solution, the iron sulphide formed is not deposited immediately but yields a greenish-black suspension, from which iron sulphide settles out only on long standing. It is also well known in analytical work that iron salts are exceptionally difficult to precipitate in presence of organic matter in general, and sugars and organic acids, such as lactic acid and tartaric acid, in particular. A latex medium, is therefore one which should tend to retard the precipitation of iron sulphide.

In order to imitate the effect of putrefaction in presence of iron prior to ammoniation, drum metal was exposed to weak solutions of lactic acid which is the chief acid developed in the natural putrefaction of latex. It was found that, if a lactic acid solution of strength 0.02 per cent. were exposed to iron for two hours, subsequently treated with excess ammonia and a little fresh latex, and then treated with a very small amount of hydrogen sulphide, a distinct discolouration developed immediately; the discolouration was still apparent after an observation period of a fortnight, during which some deposition of dark solids occurred. A control, latex—ammonia—water—hydrogen sulphide mixture showed no discolouration at all. With longer exposure of iron to stronger solutions of lactic acid and the passage of a large excess of hydrogen sulphide after ammoniation and addition of latex, the discolouration was less stable, and more pronounced deposition of solids occurred. In all cases, hydrogen peroxide and potassium cyanide discharged the discolouration as they do in a naturally discoloured latex. These experiments imitated very closely the results observed when fresh latex is allowed to stand for some hours in presence of iron before ammoniation, which then brings about immediate discolouration. Taking however the case of a latex which, although not allowed to putrefy appreciably before ammoniation, yet discolours slowly in the course of two or three weeks exposure to iron, it was necessary to show that, by exposure of iron to weak solutions of ammonia, sufficient iron could be brought into solution by alkaline as distinct from acid corrosion, to discolour fresh latex in presence of ammonia and hydrogen sulphide. Strips of drum metal were exposed to an alkaline solution containing 0.6 per cent. ammonia. The attack upon iron was very much slower than in the case of the weak solutions of lactic acid, but after approximately one week, the alkaline solution responded to hydrogen sulphide and

gave a distinct discolouration to added latex. This result again simulated the general experience with commercial latex, in which discolouration usually takes some days to make its appearance. There was now little doubt that the factors iron and sulphur bodies are together responsible for the discolouration of commercial preserved latex.

That in certain cases the degree of discolouration is limited by the available suphur bodies or iron, is instanced by two observations :—

(a) Some naturally discoloured latices, when treated with a little hydrogen sulphide, were found to show an immediate increase in discolouration, indicating the presence of available soluble iron.

(b) Eaton, Grantham and Day, (8), describe the anaerobic coagulation of latex in presence of sugars, by which process an unusually large amount of lactic acid and an unusually small amount of hydrogen sulphide are produced in comparison with a simple spontaneous coagulation. By allowing a sugar treated latex to stand in presence of iron for 4 hours, the amount of iron taken into solution should be greater than in the case of a latex containing no added sugar but the comparatively small amount of hydrogen sulphide produced, would be the limiting factor in discolouration and on ammoniation the sugar treated latex should show less discolouration than the control latex. If however both ammoniated latices were subsequently treated with hydrogen sulphide, the sugar treated latex should then show the greater discolouration by virtue of the greater available amount of dissolved iron. An experiment made to test the point. gave positive results.

It has been observed by De Vries (1) that preserved latex, which has been stored for some time, yields hydrogen sulphide on acidification, whereas this does not occur with fresh latex. The observation indicates that one effect of preservation with ammonia is the gradual production of soluble sulphides, presumably from the sulphur bodies of the proteins present. There is therefore very good ground for the theory that the discolouration of preserved latex and the formation of dark sludge, are both due to the formation of iron sulphide within the body of the latex and the experiments described have led to this conclusion. An interpretation such as this would account for the final fact that a naturally discoloured latex almost invariably has an upper layer of cream which is pure white. Allowance must be made for the fact of a high rubber content of 60 per cent. or over in this zone, with a correspondingly small proportion of the serum medium in which discolouration occurs. It must also be remembered that the surface is the only part of the latex which is exposed to air. In the light of the further experimental fact that a discoloured serum regains a good colour when exposed to air, by oxidation of the sulphide present, the fact of a good white surface cream on an otherwise discoloured latex is in no way unexpected.

Discussion

In the foregoing pages it has been shown that discolouration in preserved latex is governed by two factors

(a) the presence of soluble iron, and

(b) the presence of hydrogen sulphide or other soluble iron-reactant sulphides.

Assuming that at some time between the tapping of the tree and receipt of the preserved latex at destination, the latex has been in contact with iron for an appreciable period, then it becomes possible to account in theory for the two major observations made by buyers namely :—

(1) that one or more of the following faults—presence of coagulum, putrefactive odour, and low stability, are often associated with an unsatisfactory colour in latex.

(2) that at certain seasons of the year, the probability of a shipment reaching destination in a discoloured condition is greater than at other seasons.

With regard to the first observation, it is obvious that, if a latex is collected and allowed to reach the factory in poor condition, with no precautions against incipient putrefaction and coagulation, and if, after crude sieving, it is bulked and ammoniated, not only does it contain traces of dissolved iron and hydrogen sulphide which make for discolouration, but it also contains aggregates of globules caused by incipient coagulation and these make for poor stability. Where the amount of preservative is so inadequate that putrefaction and coagulation occur in the shipment containers, then discolouration again follows naturally upon the development of these favourable conditions. It is therefore only to be expected that discolouration is in many cases accompanied by other undesirable features.

With regard to the second observation, it is common knowledge that, at certain seasons of the year, notably after wintering, latex is unusually prone to premature coagulation which, in the absence of special precautions, pre-supposes an undue tendency toward acid corrosion of collecting vessels and formation of traces of hydrogen sulphide before the latex reaches the stage of ammoniation. The precise differences which occur in the composition of the latex are not fully understood, but it has been assumed that the content of sugars is somewhat higher than normal after wintering, which would in itself imply a somewhat more rapid development of lactic acid and a somewhat greater degree of acid corrosion of iron. It is not therefore surprising that latex shipped under present conditions seems to show seasonal variation in its degree of discolouration.

The degree of natural stability in latices from different sources provides also a possible part explanation of the fact that latex from some estates is generally received at destination in better condition

than that from other estates. It has been observed that, with certain preserved latices, which are peculiarly resistant to discolouration, the tendency towards spontaneous coagulation when in the unpreserved condition is less than average and it is therefore to be supposed that the degree of acid corrosion of vessels between tree and factory is also small. It has been confirmed with one such latex, of which trial shipments have reached America in excellent condition, that the ash of the fresh latex at the time of arrival at the receiving station, contained no qualitatively detectable amount of iron. After ammoniation, if discolouration is to take place in transit, the necessary iron must be brought into solution purely by alkaline corrosion which has been shown to be much slower than acid corrosion; similarly, since little or no putrefaction has taken place before ammoniation, the slow development of soluble sulphide, which appears to take place in preserved latex by the alkaline hydrolysis of protein material, is now the sole source of this essential factor and is not merely an accessory, supplying an additional quota to the amount which might in other circumstances be present before ammoniation. It is further not beyond the bounds of possibility that latex owes its natural stability, at any rate in part, to the resistance of its proteins to decomposition, so that a latex of high natural resistance to spontaneous coagulation, would be less liable to discolouration in transit than one of low resistance. It is very probable that the natural stability factor is important in this connection, though it is clear, from the putrefaction experiments described, that even a very resistant latex can be caused to discolour very rapidly if too much time is allowed for decomposition in presence of iron before ammoniation; thus, under present conditions, an estate of which the latex shipments show a good white colour, may also owe part of its success to the arrangements governing the length of time between collection and final ammoniation, or alternatively to arrangements for very early ammoniation in the field.

It is clear that since every contact of latex with iron, whether the latex be in the fresh or in the preserved condition, carries its dangers, the ideal of production would preclude contact with iron at every stage between tree and buyer; it would either abolish completely every iron vessel whether used for collection, storage or transport or, in the alternative, cause every iron vessel to be so treated on its surface with wax or with some carefully selected variety of paint-like coating, that direct contact of latex with iron, was rendered impossible. Although it is true that the steel drum commonly used for latex shipment is now shown to be unsatisfactory for the purpose, and although the best alternative is bulk shipment from waxed storage tanks to waxed steamer tanks which, by reason of their surface protection and by reason of the smaller ratio of surface area of container to volume of latex, approach very near to the

ideal, much latex must of necessity yet be shipped in the unsatisfactory drum; the wooden barrel presents an obvious advantage over metal drums, in that it contains no iron, and it is not easy to decide whether the reluctance shown up to date by practically all buyers to accept latex so shipped, is not based more on prejudice than on some firmly grounded reasoning against it; containers of stainless steel or other resistant metals must at present be ruled out on account of cost; the brand new kerosene tin, by reason of its tinned coating, possesses a clear advantage, and, although in certain other respects it is perhaps not acceptable to buyers, it yet merits consideration from the point of view of retardation of discolouration; the ready assembled steel drum, whether new or second-hand, having no interior protective coating, is not only unsatisfactory by reason of the absence of such coating, but also by reason of the fact that it is only with extreme difficulty that the estate can apply a protective coating, and even then the coating cannot be guaranteed to be either uniform or continuous. The treatment when attempted, is extremely wasteful of time and material. Since however no new drums, which have been given a satisfactory internal treatment before assembly, are at present on the market, it seems that the present unsatisfactory state of affairs must inevitably continue for some time; many shipments of latex must yet reach destination in a more discoloured condition than would be the case if the really satisfactory and at the same time cheap container which is probably one of the greatest immediate needs of the latex industry had been standardised and had become available.

To the argument that, since no satisfactory container is yet available, it is useless to take precautions at other stages in production, the answer is that it is now shown to be more than ever incumbent upon the producer of latex, to devote very great care indeed to its preparation, since it is now apparent that a great deal of the trouble may have become potentially if not visibly present between tree and factory; possible sources of iron contamination, in this short stage of the history of the latex, are numerous, and include the dirty latex cup containing iron-bearing soil, the collection pail and/or the larger transport vessel; if semi-clean, bacteria-fouled pails, and other primary transport vessels, which act as accelerators of spontaneous coagulation, are used in the absence of ammonia as an anti-coagulant, the resulting slight acid corrosion may, in conjunction with the later effects due to the container itself, make the difference between a passable latex and a latex showing serious discolouration. It therefore behoves the producer, who is admittedly working at a disadvantage, to take every possible precaution against unclean vessels, careless collection and incipient coagulation between tree and factory. In the field, for a long transport to factory, the advantage of the use of a small quantity of ammonia is obvious. Sodium sulphite solution is not to be recommended for the purpose. Investigation is being made

of the most suitable media for coating, collecting, transport, bulking and storage vessels.

Where estates ship, as a single monthly consignment, the accumulated crop of a whole month, it is at present the exception rather than the rule to find a storage tank sufficiently large to hold the whole bulk; it is usual to find tank space sufficient for only one day's crop. The effect of such a paucity of tank space is that the latex must be filled into the transport drums daily, and the latex in some drums is therefore in contact with iron for almost a whole month before shipment, while other drums of the same consignment contain freshly packed latex. Buyers often report that in a single monthly consignment, great variation of colour occurs between drum and drum. In the light of the present experiments, the explanation is obvious and with it the need for large estate storage tanks which can be adequately coated internally with wax or other suitable medium; storage of the accumulating consignment can by this means be achieved without undue contact with iron and monthly shipments can be expected to show not only uniformity in colour, but also an improved colour. The large storage tank lends itself also to the removal of some undesirable material from the latex before shipment.

The experiments, in their indication that part at any rate of the phenomenon is colloidal, would lead at once to the conclusion that the attempt to re-condition an already badly discoloured latex by centrifugal clarification, would be only partially successful, in that only the coarser precipitable sulphide would be removed. Experiments made at the Institute had already given indications that such was the case and in a private communication from a large American buyer, extensive experiments are described which supply full confirmation that centrifugal treatment is in fact only partially successful. It would be fallacious to argue however, that a centrifugal clarification of freshly preserved undiscoloured latex, aimed at the removal of dirt, rust flakes from containers and other impurities, is not a desirable estate measure.

Until such time as the ideal container becomes available, it will clearly be impossible for the estate to guarantee that a latex, having a good colour at the time of shipment, will also be of good colour on arrival at destination and in the drafting of latex contracts specifying a type of container and at the same time a latex of good colour, considerable caution is therefore advisable.

Estates are warned that the use of hydrogen peroxide and potassium cyanide must not be adopted except at the direct and specific request of the buyer.

Summary

Discolouration in preserved latex is attributed to contamination with iron and to the presence of hydrogen sulphide or soluble iron-reactant sulphides.

Acknowledgements

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