

A thesis, presented to the Department of
Chemistry of Union College, in partial fulfill-
ment of the requirements for the Degree of
Bachelor of Science in Chemistry, by

Angelo J. Sederus

Approved by _____

May 21, 1940

UN⁸92
S44
C.2

PREVENTION OF BLEEDING
by the
COATING OF THE PIGMENT PARTICLES

A. HISTORICAL

Specific information pertaining to research work on the "bleeding" effect of certain pigments proved very difficult to obtain. The historical background of this thesis, therefore, will have to be confined to a general description of previous work obtained from correspondence with A.F. Brown, General Manager of the Pigment Division of the Imperial Color and Paper Corp., G.G. Sward of the National Paint Varnish and Lacquer Association, and E.R. Allen, Technical Director of Kiebs Pigment and Color Corp. The bleeding of a pigment like Para Red in a vehicle such as linseed oil or petroleum thinners is fundamentally due to the fact that Para Red is soluble in such mediums. For one reason or another, a great deal of work has been done with protecting agents. It is perfectly feasible to coat the surface of pigments, so that they will wet differently and grind differently, but to date none of these agents have shown promise to prevent solubility of a pigment. The present method used to prevent bleeding is to coat the bleeder layer with a coat of dewaxed shellac before applying the final finish .

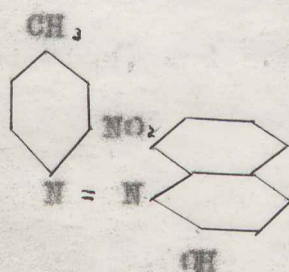
B. PURPOSE OF RESEARCH

The problem, essentially, is to conceive of a treatment which such a pigment could be given that will render it insoluble in those mediums in which it bleeds, without changing its characteristics in some other respect or making it so costly to manufacture that it would be impractical.

C. SUMMARY OF PIGMENT DESCRIPTIVE MATERIAL:

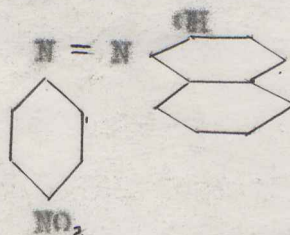
Toluidine Red, Para Red, and Tungstate Victoria Blue Pigment were taken as good examples of bleeding pigments. The formulas for these pigments are as follows:

1. Toluidine Red is made by coupling meta-nitro-para toluidine with beta naphthol



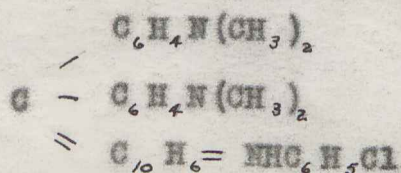
Toluidine red

2. Para Red is made by coupling para nitro-aniline with beta naphthol



Para red

3. Tungstate Victoria Blue is made by the precipitation of Victoria Blue with tungstic acid



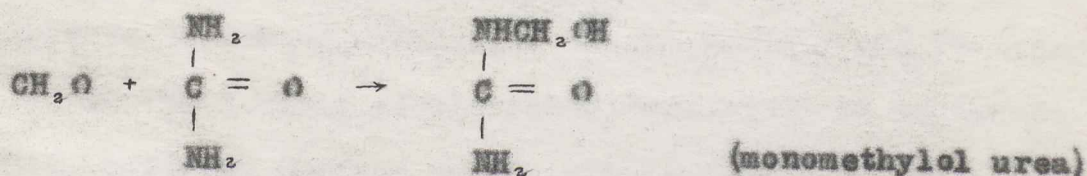
Victoria Blue

D. SUMMARY OF UREA FORMALDEHYDE DESCRIPTIVE MATERIAL:

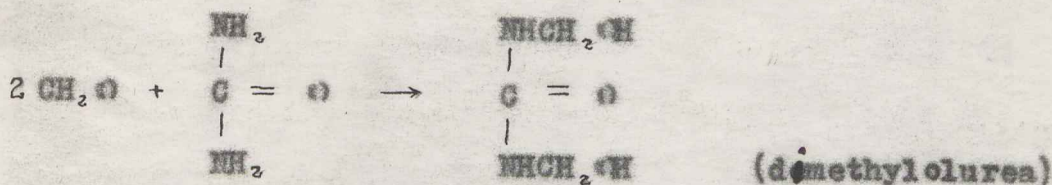
In an aqueous medium, numerous investigators seem to be more or less agreed on the general principles underlying the reactions of urea and formaldehyde. In general, the resulting condensation product is dependent upon:

1. the catalyst employed including the pH of the solution as a catalytic factor.
2. the molecular ratio of the reacting components.
3. the time and temperature of the reaction.

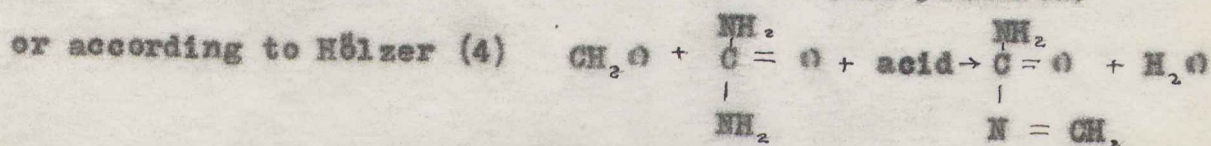
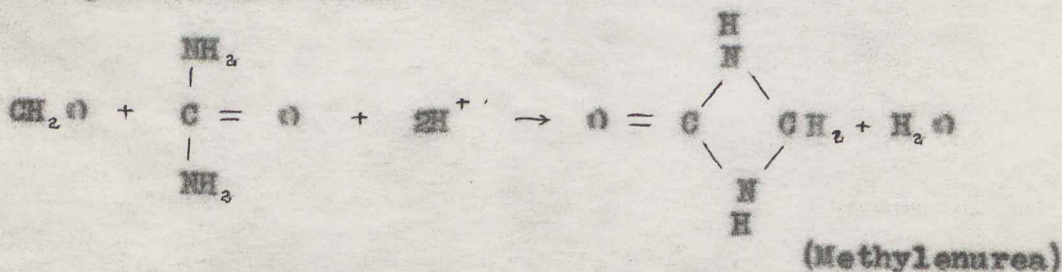
With one mole of urea and one mole of formaldehyde in the presence of hydroxyl ions, monomethylol urea is formed.



When an excess of formaldehyde (i.e. one mole of urea and two moles formaldehyde) is employed, dimethylolurea is formed.



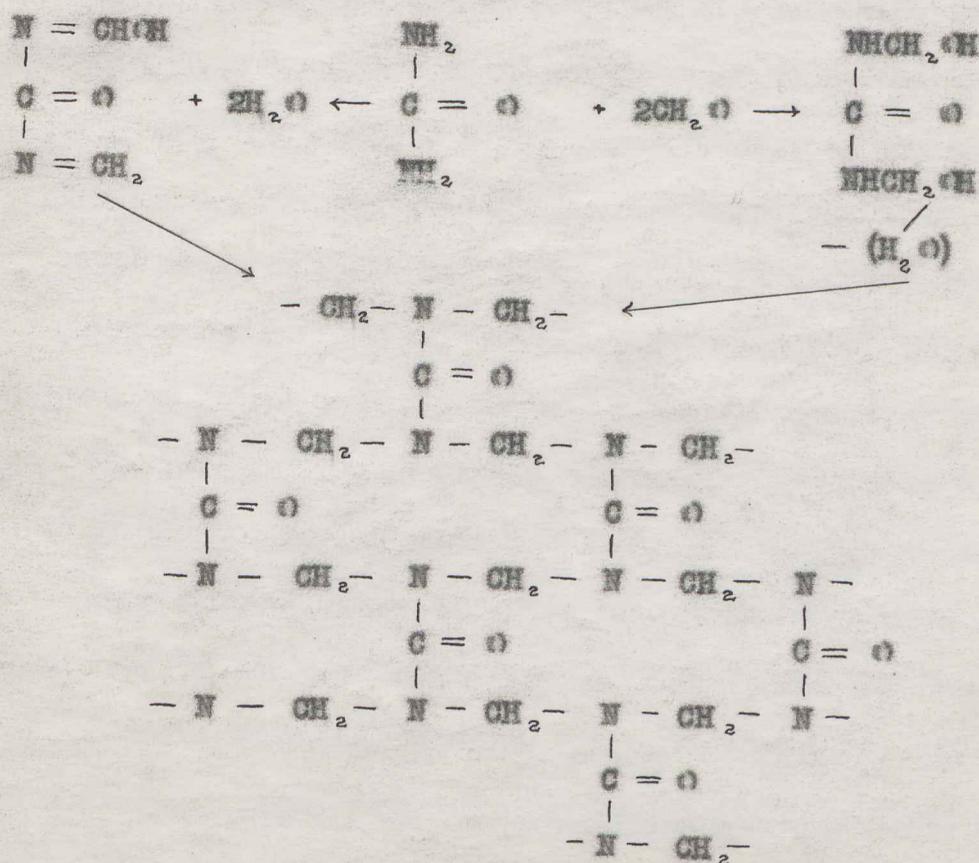
In the presence of dilute acids, a white amorphous precipitate is formed.



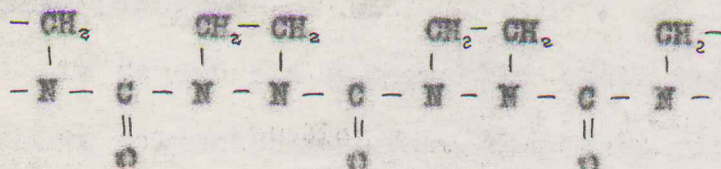
The mechanism of reaction has had many interpreters. There appear to be two possible mechanism by which the final end product from the reaction of one mole of urea and two moles of formaldehyde is obtained.

1. Condensation thru the demethylolurea intermediate
2. Polymerization thru the demethylolurea compound

There are two very distinct types of reactions. In a polymerization reaction the reactants are generally marked by a large degree of unsaturation and the resulting more saturated polymer is a multiple of the initial reactants, in other words the percentage composition remains unaltered. In condensation reactions, on the other hand, the final product is no longer a multiple of the monomer and in order to obtain the formula of the final condensate it is necessary to subtract the sum of the simple compounds which have been liberated during the condensation.



The hypothesis is advanced by Redfarn (5) that resin formation takes place according to the polymerization of dimethylol urea as a saturated chain.



This appears to be quite improbable because such structure indicates linear polymers which according to resin theory would be a best non-convertible resin. The case, however, is that urea formaldehyde polymers definitely behave like three dimensional units because irreversible gel structure is obtained on continued heating. Gelation is not accounted for unless it is shown that cross linkages occur by the reaction of additional molecules to tie in at some other place between the linear polymers.

If the resulting molecules were all dimethylolurea (possible when starting with one mole of urea and two moles of formaldehyde) instead of an equal number of molecules of dimethylolurea and monomethylol urea (possible when starting with two moles of urea and three moles of formaldehyde), the chance probability of reacting molecules in the three dimensional space appears to be highly in favor of the first structure shown. Since monomethylolurea has three reactive hydrogen atoms and one reactive hydroxyl group, it appears that, even if monomethylol urea alone were involved without any molecules of dimethylol urea, it should still be possible to form cross linkages between linear structures and account for best convertibility. As dimethylolurea is generally

present with monomethylolurea this greatly increases the chances of forming complex structures and expediting heat convertibility.

It is not yet universally known that urea formaldehyde coating compositions are essentially polymerizing rather than oxidizing resins, although this point has been often emphasized. More recent discoveries, however, have shown that by the introduction of special acidic catalysts, these urea formaldehyde resins may be rendered not merely convertible at a much lower temperature than they have previously been baked, but also may be made to dry in a few hours to clear, transparent, glossy, hard, glasslike finishes, ready to sand if necessary.

Since urea formaldehyde resins set essentially by polymerization rather than by mere evaporation of solvents and certainly not by oxidation, in general, the higher the baking within limits, the better are the results. The setting also depends on the pH of the system - i.e., the effect of pigments, plasticizers, and solvents used in the formulation. In order to ensure hardness from lower temperature bakes, the system should be slightly acidic.

The effect of the acidity or alkalinity of the pigments, as measured by the change in the hydrogen ion concentration because of the pigments, upon the results obtained in coating compositions containing urea formaldehyde resins has not been completely studied. Enough is known, however, to permit the generalization that those pigments or pigment com-

binations, which cause a pH below 7, increase the reactivity and decrease the time necessary for conversion from sol to gel, a conversion for which urea formaldehyde resins are noted; conversely, pigments or pigment combinations, the pH's of which are above 7 have a tendency to lower the reactivity and lengthen the time necessary for conversion of the urea formaldehyde component.

During earliest stages of urea formaldehyde condensation the products are soluble in water or in the formalin solution employed. The reaction product is at that stage, therefore, a hydrophilic colloid. On further condensation, however, the hydrophilic becomes a hydrophobic and hence is insoluble in water. There is a tendency for urea resins in lower stages of condensation to become converted gradually and spontaneously to a more highly condensed substance, so that a product which at one time is soluble in a given medium will later be found insoluble, to improve the solubility of well condensed urea resins in organic solvents and also to prevent the progress of further condensation after application, one development of manufacture comprises reacting urea and formaldehyde in the presence of an alcohol with the object of having the alcohol unite in the resin and confer solubility and stability.

DESCRIPTION OF WORK CARRIED OUT AND RESULTS:

In addition to the economic aspects of the problem, mechanical difficulties arose. One is that the resin coating applied to the pigment might have to be of such magnitude that the properties of the system would be unduly

altered. Another is that organic pigments of this sort will not stand high heats without decomposition, or at least loss of brilliancy.

There are two obvious methods of attacking this problem. One is to precipitate the pigment initially in the presence of the resin medium and then carry out the process of filtration, drying, and grinding. The other is to apply the resin coating to the pigment particles after they have passed through the production treatment. Since it was believed that enough information might be obtained from resulting observations to tell whether or not the idea was worthwhile, the latter procedure was chosen because of its greater adaptability to laboratory facilities, financial resources, and information on the subject.

A standard test as to whether or not a pigment bleeds is to simply put one gram of dry color into 100 cc of solvent, soak for twenty four hours, shaking occasionally, then filter and observe whether or not the filtrate is stained. A slight stain does not necessarily mean that the color will bleed sufficiently to cause trouble. Where the stain is not very pronounced, before rejecting the color, it is well to make up a small amount of lacquer and then stripe with white. The first thing done was to actually test the Toluidine red, para red, and tungstate blue pigments for bleeding by means of the solvent method. Then panels were coated with lacquers containing the respective pigments. After they had dried a few stripes of a white lacquer were applied. The bleeding

became apparent within a few minutes after application.

The lacquers used were air dry lacquers of the following composition:

Clear lacquer

Total Solids	35%
Volatile Thinners	<u>75%</u>
	100%

Solid Matter

Nitrocellululose	34%
Synthetic Resins	16%
Shellac	14%
Ester Gum	22%
Caster oil	<u>14%</u>
	100%

Volatile Matter

Butyl alcohol	20%
Butyl acetate	10%
Ethyl acetate	10%
Ameyl acetate	20%
Toluol	<u>40%</u>
	100%

The white lacquer was prepared from the clear lacquer by using Titanium Dioxide as the pigment.

As a precaution the lacquer applications were allowed to dry for at least six hours before any attempt was made to stripe them with the white lacquer.

It was thought advisable to determine how high a temper-

ature the pigments might be raised to without changing their properties in anyway. Accordingly, samples were enclosed in pieces of thin glass taping and by using the Thiele Tube apparatus the temperature was raised to 200 C with no apparent effect on the pigments. This temperature limit was set there-upon to apply to all further experiments carried out.

Further tests were conducted as to the solubility of the various pigments in different mediums. The results are tabulated below:

I. Solubilities in H_2O

P.R. - Practically insoluble

T.R. - Slightly soluble

T.B. - Slightly soluble

II. Solubilities in n-Butyl acetate

P.R. - Quite soluble

T.R. - " "

T.B. - " "

III. Solubilities in Toluol

P.R. - Quite soluble

T.R. - Not as soluble as P.R., but still quite soluble

T.B. - Same as T.R.

IV. Solubilities in Formalin

P.R. - Practically insoluble

T.R. - Practically insoluble

T.B. - Very soluble

V. Solubilities in 1 N NaOH

P.R. - Soluble

T.R. - soluble

T.E. - soluble

In attempting to evolve a suitable protective resin coating several resins were prepared. Urea formaldehyde, because of its insolubility in most organic solvents and because of its solubility in water and alcohols seemed the most promising of these. There were numerous "failures" in so far as applicability of some of these resins were concerned, either because of the rigidity of the cooled resins, their brittleness or extreme hardness, or because of their discolored appearance.

A flexible alkyd resin was prepared by mixing 20 grams of glycuol, 25 grams of pthalic anhydride, 10 grams of ethylene glycol, and twenty grams of succinic acid together. This mixture was heated to a temperature of 190 to 200 C. Small amounts were removed from time to time with the spatula to observe whether the mixture would solidify upon cooling to give the desired product. When the resin had been heated sufficiently it was poured into a beaker. Small portions were mixed with sample of the different pigments and these were allowed cool; they hardened. The resin upon being tested proved to be soluble in the lacquer solvents and as a result the bleeding of the pigments was not checked.

In addition a phenal formaldehyd compound was formed by mixing 10 parts of phenol with 7.5 parts of ordinary

formalin and a little ammonia. This mixture was heated at 80-90 C under a reflux condenser. After the resinification had occurred, the water liberated from the formaldehyde solution was boiled off. This substance altered considerably in fusing point when drying and in doing so it became less soluble and less fusible. This resin also proved to have little effect as far as prevention of bleeding was concerned.

A Furfural resin also was tried. A solution of 3.5 parts of NaOH (28.5%) was heated to the boiling point under a reflux condenser. One part of a mixture of equal volumes of furfural and acetone was added slowly over a fifteen minute period. The boiling was continued fifteen minutes after this addition. The resin was washed while it was still hot with water acidified with HCl and the resin was ~~then dried~~. This compound proved to be soluble in water and organic solvents as well and consequently it proved to be a failure as regards protective effect on pigment particles.

Several preparations for urea formaldehyde resins were employed. Some of these were discarded because the end product was undesirable and others because of their instability.

1. The ratio of the reactants was 50 parts of urea to 120 parts of formalin. The formalin was first heated from 90 to 95 C under a reflux condenser and 10 parts of urea then added. It was then heated to boiling and as soon as

the ebullition started the heat was removed. Since the reaction is exothermic it is not necessary to use additional heat. The urea is added 10 parts at a time until it has all been added. The resulting liquid is thin and colorless and upon cooling it sets to a stiff gell. Upon standing it synerizes.

2. Another preparation using 15 parts phthalic anhydride 15 parts of urea and 60 parts of 40% formaldehyde was carried out. This mixture was boiled from twenty to thirty minutes. A white precipitate formed the final end product upon standing for a few hours.

3. A glass like product was obtained by mixing 100 g. of 30% formalin, 20 g. of urea, and a few cc of dilute HCl and then heating the mixture at 100 C for awhile. Upon cooling, the liquid set to a gel and gradually hardened.

4. Urea (10 parts) and 60 parts formalin were refluxed for 15-60 minutes. This gave a syrupy product which was diluted with an equal volume of acetone or some furfural. A lacquer was prepared by mixing this with nitrocellulose.

5. Another urea formaldehyde coating composition was obtained by refluxing 30 parts urea with 100 parts formaldehyde. After about 15 minutes, 5 parts of boric acid dissolved in a little water, were added. On standing in the cold for several hours, two layers were found to separate. The upper one was removed and the gel forming lower layer was washed repeatedly with water and then dissolved in a non aqueous solvent such as acetone.

In applying the resins to the pigments two procedures were open. One was to precipitate the resin on the pigment by having the pigment present in the reaction flask. The other was to prepare the resin and then add the pigment, thoroughly wetting the particles with the resin solution. No noticeable difference was observed in the effect on the properties of the pigments by these two procedures excepting in the case of the tungstate blue. Because of its solubility in formaldehyde the presence of the tungstate blue in the reaction flask is disadvantageous.

After the pigments and resin solution had been thoroughly mixed together they were allowed to stand for several hours until the mixture had gelled. This was then dried, ground with a mortar and pestle and subjected to the aforementioned tests for bleeding. Although it was evident from the start that in grinding the pigment-resin precipitate the resin coating must be removed from some of the pigment particles, it was difficult to believe that the urea formaldehyde was not coating a majority of the pigment particles. According to the results of the bleeding tests, however, the pigments were not made any more insoluble than they had been originally.

The idea suggested itself that perhaps the use of a lacquer (heat hardenable) forming a harder coating than the air dry lacquer formerly used might be employed. It was also decided to write to certain companies for any information they cared to give out concerning work they

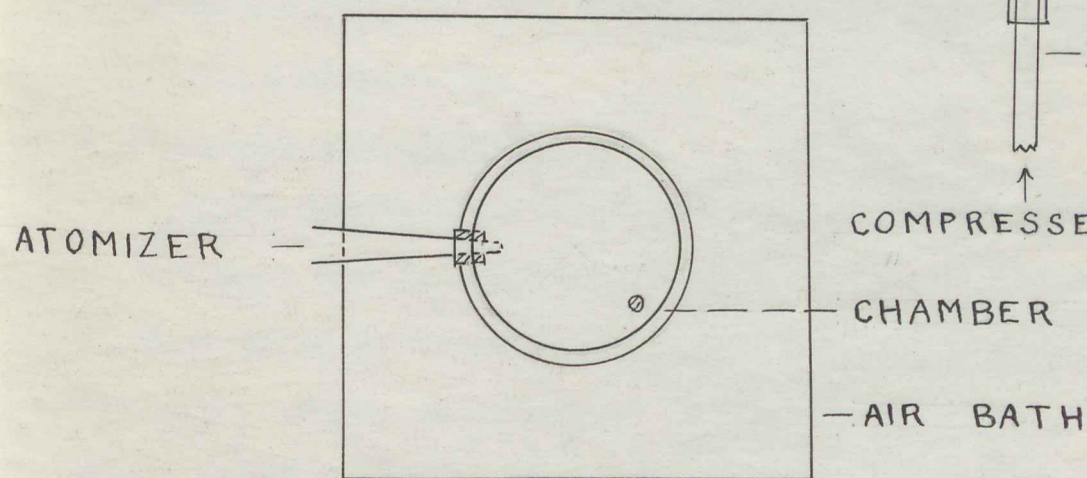
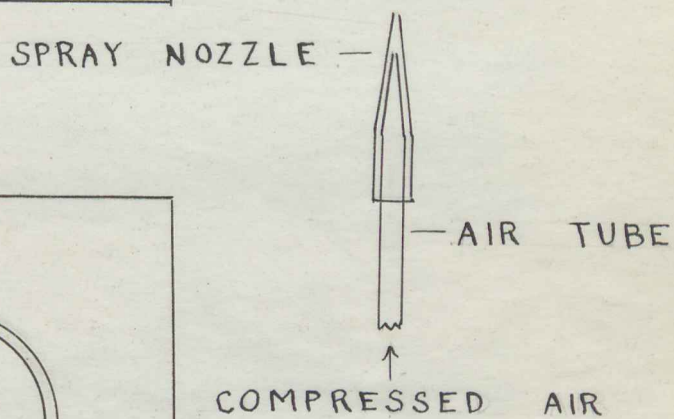
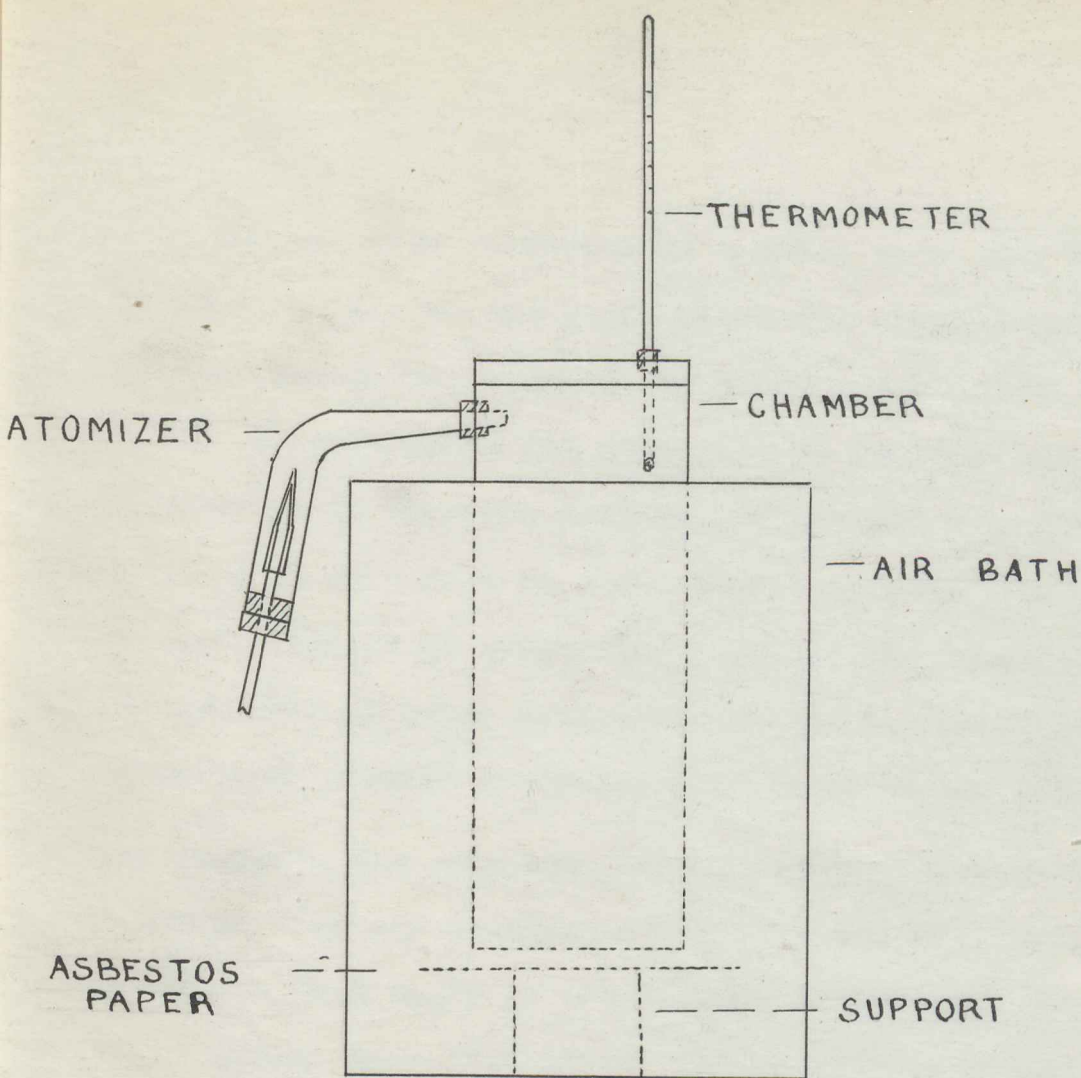
might have done on bleeding. The results were rather discouraging. A sample of a resin (heat hardenable) was received from the Bakelite Corporation, however. This resin, XL 8778, and a Bakelite solvent, X5305, were used in preparing a lacquer which although far from a perfected product, still served its purpose. This lacquer was used with untreated pigments to make up pigmented lacquers. The applications were baked for forty minutes at 110 C. On being striped the pigments bled. The next step was to take some resin treated pigment and use that with some of the heat hardenable lacquer. In this way it was believed that the heat absorbed would not only harden the lacquer film but it would also aid the polymerization of the urea formaldehyde and make the protective particle coating tougher. When this coating was tested for bleeding the improvement was very noticeable.

Up to this time preparation #1 for urea formaldehyde was used. It is suggested by Ellis (1) that the gelatinization of the water soluble condensation product which forms an intermediate stage in the resin condensation is accelerated by the addition of electrolytes. There is one group of electrolytes that rapidly converts the initial soluble product into hardened insoluble resins. Generally speaking the ammonium salts comprise this group. Another division containing the mineral acid salts of the metals, exerts no hardening action but it does accelerate gelatinization.

It was found that a higher ratio of formaldehyde to urea yielded clearer gels, a slightly acidic medium also helped clarity of the viscous solution, and NH_4Cl accelerated the gelation. It was also observed that if the resin solution was kept in air tight bottle it could be kept for quite a long period of time in a stable form. A reproducible urea formaldehyde resin was finally evolved. This was prepared in the following manner:

10 parts of urea were added to 60 parts of 37% formalin and a few cc of dilute HCl . The mixture was refluxed at 100°C from 15-60 minutes. The resin solution was made 2% in concentration of NH_4Cl and the mixture allowed to cool in an airtight flask. Samples of it were allowed to gel and tested for solubility in organic solvents. The resin proved to be insoluble in the common organic solvents. This preparation was used throughout the balance of the work on the urea formaldehyde protective coating.

The more work that was done on the problem the more ^{was} it seemed that the essential question, and still is, how to coat the pigment particle completely with a hard, insoluble, incompatible coating. The idea of spraying a pigment-resin solution mixture into a current of hot gas seemed to have the highest probability of insuring the complete coating of the pigment particle. In this way the solvent would be evaporated and the coated particles deposited. A simple apparatus was arranged to attempt to carry this process out on a small scale.



The air bath consisted of a metal can. The idea was to heat the air to the point where the chamber would be at the temperature desired, by heating the bottom of the bath. At this point the atomizer was inserted and the pigment-resin solution mixture was sprayed into the chamber. Runs were made at temperatures ranging from 110 to 150 C spaced at intervals of 10 C. The temperature was capable of being controlled within 5 . Although small amounts of pigment particles were found in the bottom of the chamber, the apparatus on the whole proved to be a failure. The air pressure of 10 lbs. was not high enough to give a fine spray of the suspension and most of the spray merely deposited itself on the side of the chamber opposite the atomizer. This was tested for bleeding along with the residue at the bottom and both of the samples bled in arc; test. The atomizer, itself did not prove entirely satisfactory.

CONCLUSIONS AND SUGGESTIONS:

It is regrettable that time did not permit further development and experimentation with the spray apparatus because spray driers have already proven their worth in industry. There is no reason to believe that the pigment-resin solution could not be sprayed with a suitable atomizer to give droplets of fairly regular size. A lower boiling solvent could be used in the place of water and this would accelerate the rate of drying of the resin coating on the pigment particles.

Regulation of the factors involved would assure a final product consisting of the unagglomerated pigment particles.

The most important direct result from this work was the illustration that the bleeding could be prevented to a considerable extent, without covering the bleeding layer with a coating similar to shellac before striping with white. This was done by using a urea formaldehyde coated pigment with a heat hardenable lacquer. This proves that the urea formaldehyde actually had a protecting effect on the pigment but that it was necessary to harden or "cure" the resin in order to derive the maximum benefit from its application.

The accumulated observations and results point to the two methods of approach suggested in the beginning of this article. A summary of the requirements for the protective coating might make them clearer.

1. The protective coating must completely cover the pigment particle.
2. This coating must be insoluble in the lacquer solvents.
3. It must also be incompatible with the resins used in the lacquer to prevent its solution by them.
4. It must be easily applicable.

The first of these requirements is perhaps the most important at the present stage. One way to assure the complete wetting of the pigment by the resin is to actually

precipitate the pigment in the presence of the resin solution at the start. Another is the spray drier method. One difficulty in this method might be that the resultant particles would be so fine it would be difficult to have them settle to the bottom of the chamber.

It is obvious why the coating must be insoluble in solvents. Urea formaldehyde is particularly outstanding in this respect. It should also be incompatible with the other resins used in the lacquers or else the purpose of the protective coating would be defeated by its solution in the lacquer resins.

The last requirement is an economical as well as a mechanical necessity. The urea formaldehyde is fairly cheap to manufacture and can be used in a form that permits of easy application. The concentration of the urea formaldehyde in its solutions can be easily controlled and varied. In addition the solutions are uniform and stable.

In conclusion, it is only fitting to say that it is the hope of the author that this work has opened the way for a solution of the problem of bleeding pigments and that it indicates increased use of urea formaldehyde, not only in lacquers, but in the field of coated pigments.

ACKNOWLEDGEMENTS:

The author wishes to acknowledge and thank Messers A.F. Brown, Imperial Color Works, Glens Falls, N.Y. for his cooperation in supplying sample pigments, and William

Wright, United Lacquer Co., Linden, N.J. for his technical advice and his assistance in obtaining lacquers. Thanks are also due to Mr. C.F. Grief, Bakelite Corporation for the resin samples he was instrumental in obtaining for this work.

BIBLIOGRAPHY:

1. C. Ellis - "THE CHEMISTRY OF SYNTHETIC RESINS",
Vol. I. p. 597
2. T.S. Hodgins and A.G. Hovey - "INDUSTRIAL AND ENGINEERING CHEMISTRY", 30, pp. 1021-9, 1938
3. T.S. Hodgins, A.G. Hovey and P.J. Ryan - "INDUSTRIAL AND ENGINEERING CHEMISTRY", March 1940,
pp. 334-345
4. Hölzer - BER., 1884, 17, 659, 1885, 18, 3302
5. C.A. Redfarn - "BRITISH PLASTICS", 1933, 5, 238,
CHEM. ABS., 1934, 28, 1555