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Nathan William Muller
University of Louisville

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UNIVERSITY OF LOUISVILLE

FACTORS AFFECTING THE BRONZING OF PRUSSIAN BLUE PIGMENTS.

A Dissertation
Submitted to the Faculty
Of the Graduate School of the University of Louisville
In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF CHEMICAL ENGINEERING

Department of Chemical Engineering

by

Nathan William Muller

1939

FACTORS AFFECTING THE BRONZING OF PRUSSIAN BLUE PIGMENTS.

Approved by Examination Committee:

Director: ______________________________

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Approved for English:

June 6,1939

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Author Wishes

to Acknowledge His

Appreciation

for All the Kind and Valuable Aid

Given by Dr. G. C. Williams,

Who Directed This Research

INTRODUCTION

In recent years the widespread use of lacquers in the automotive industry created a demand for a type of blue pigment which has not yet been produced. It must have all of the properties of the printers' blue except one- i.e. the reddish cast. A total elimination of bronziness from printers' blue while the other properties were retained would result in an ideal lacquer blue, for this blue pigment would then have the following properties:

1. brilliancy of color,
2. ease of dispersion and wetting in the oil or solvent medium,
3. a high tinting strength,
4. softness and ease of grinding,
5. blue top-tone and over-tone without any trace of bronze or red cast by either reflected or transmitted light.

With these things in view, this research was undertaken to investigate the variables which might affect the bronzing tendency of the pigment.

HISTORICAL

The discovery of Prussian Blue is credited to Diesback, a German color maker, who in 1704 discovered the blue accidentally. He was making a lake with copperas and an impure potash containing some bone distillate. His process was kept secret, but in 1724 Woodward published a paper in the Philosophical Transactions demonstrating how a similar pigment could be made by calcining blood with caustic potash and treating the extract with copperas, alum, and acid. For many years this was the sole method whereby Prussian Blue was produced.

Almost a hundred years passed before any comprehensive investigations were carried on in the chemistry and structure of these blue pigments. Scheele, Berthollet, Gay Lussac, and many others were connected with this work, and the terminus has not as yet been reached.

Commercial exploitation of the pigment was begun in Germany and in 1770 started in England (56). At that time the price was $ 11.22 per pound (2 Guineas) yet seventy years later the price has been gradually lowered to $ 0.34 per pound, which is comparable to the present day cost. The development of the process for the recovery of cyanides from gas producers and the direct conversion of these cyanides to Prussian Blue created the present day price level.

At the outset of the World War in 1914 the price of potash increased so much that the pigment makers began looking for a cheap substitute which could replace the potassium in the processing of pigments, dyes, and lakes. Sodium compounds were not only cheaper, but resembled those of potassium in chemical and physical properties. The color maker soon found that the prussian blue pigments made from sodium ferrocyanide alone were much inferior to those made from the potassium salt (56). It was found that a part of the potassium could be replaced by sodium without affecting the quality of the product (18) and this substitution afforded a substantial saving. The desirability of gas producer wastes as a raw material was traced to impurities of ammonia and subsequently led to an ammonia-soda blue pigment which even surpassed the original potash blues. At the present time only very small quantities of potash blue are made, and these are for special purposes rather than for general use.

As the investigation of the chemical and physical properties progressed, so did the production of variations from the original. There soon was developed a type of blue pigment which was especially desirable to the printing industries. It was characterized by a high degree of covering power and tinting strength, delicate shadings, low oil absorption, and a definite red cast. This series was known as Printers' Blue, Steel Blue, Milori Blue, and Bronze Blue.

The next development was Chinese Blue, a pigment desired by the manufacturer of enamels and paints. The group has a lower tinting strength, increased hardness, and a green overtone replacing the reddish cast. At the present time industry demands both types of blue.

THEORY

According to Bancroft (3) the color of any pigment is influenced by two conditions. These we may classify as pigmentary and structural. " Pigment" colors are those which we see by the light transmitted from the pigment to the eye, where the absorption of light is dependent upon the molecular structure of the material. " Structural" colors are those colors or parts of colors which are caused by, or modified by, the physical structure of the pigment. The latter classification includes colors of pigments and dyes which have been termed dichroic, that is, possessing of more than one characteristic color. Some pigments may be dichroic because of changes in particle size (3)(20)(42)(60).

Pigmentary Effects:

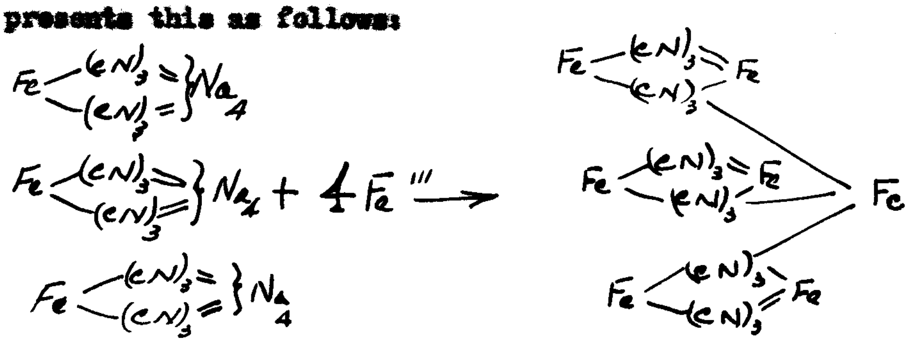
The reaction between sodium ferrocyanide and ferric chloride may be represented by the equation (56):

$$3Na_4Fe(CN)_6 + 4FeCl_3 \rightarrow Fe_4[Fe(CN)_6]_3 + 12NaCl.$$

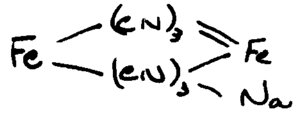
This has been substantiated by the decomposition of the prussian blue with sodium hydroxide as follows:

$$Fe_4[Fe(CN)_6]_3 + 12NaOH \rightarrow 3Na_4Fe(CN)_6 + 4Fe(OH)_3$$

The reaction between a ferric salt and sodium, potassium, or ammonium ferrocyanide may be considered as the removal of the Na', K', of NH_4' from the ferrocyanide, the grouping of six of these molecules, and combination with the trivalent iron as their nucleus. Justin-Mueller (24) represents this as follows:



In the production of prussian blue the complete reaction is not attained. Practically, all the original sodium, potassium or ammonium is never removed and the partial products lie between the limits of $Fe'_3(Fe(CN)_6)_4$ and $Fe''M'Fe(CN)_6$. The substitution of sodium by the replacement of trivalent iron from the nucleus of the triferri-ferrocyanide produces a soluble blue. This replacement may result in a structural formula as:



Justin-Mueller (24) produced the corresponding acid by treatment of the original with oxalic acid. The formation of this compound might account for the solubility or peptization of prussian blue in the presence of excess ferrocyanide.

The consideration of a structural formula for prussian blue indicates that:

1. The $(CN)_3$ groupings are not the chromophoric groups in the molecule, but are intensifiers or auxichromes, as the ferrocyanides of sodium, potassium, ammonium, calcium, and lithium are only slightly colored, and the free acid is white (56).

2. The internal iron (Fe") is not the color forming group since its replacement by platinum in the molecule may produce sodium, potassium, ammonium, and calcium platinocyanides which are closely related to the ferrocyanides in color and structure (44)(55)(56). The intermediate white paste contains merely the ferrous iron and becomes colored

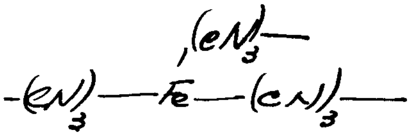
only on oxidation.

3. Since the $Fe^{\prime\prime\prime}$ iron is the only other member in the molecule it remains as the only material left to be the chromophore group.

In the structure of the blue pigment, according to Justin-Mueller, there occur two definite $Fe^{\prime\prime\prime}$ groupings, namely:

$$—(CN)_3—Fe=(CN)_3—$$

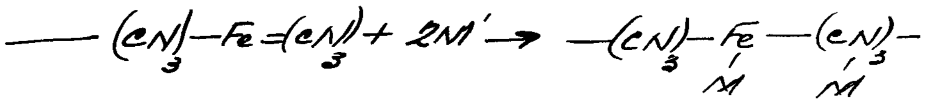
and



$$-(CN)_3—\underset{\textstyle (CN)_3—}{\overset{\textstyle (CN)_3—}{Fe}}\!\!—(CN)_3—$$

The chromophore may be either one or both these groups.

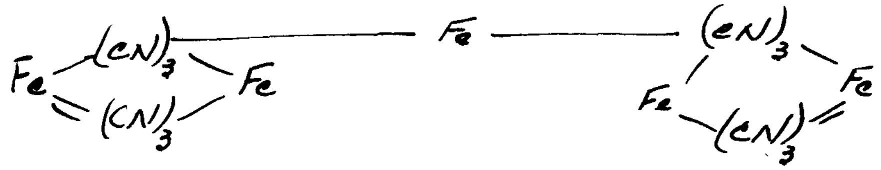
It has been found that the replacement of part of the formal weight of $Fe^{\prime\prime\prime}$ by $Na^{\prime}$, $K^{\prime}$, $NH_4^{\prime}$, $Cu^{\prime\prime}$, $Pb^{\prime\prime}$, and $Mn^{\prime\prime}$ has a marked effect upon the color of the resulting pigment and in some cases $NH_4^{\prime}$ has acted as an intensifier of the color (18)(56). The introduction of an ion such as $M^{\prime\prime}$ or $M^{\prime}$ may be accomplished by breaking the double bonded valence between the iron and the cyanogen groupings thus:



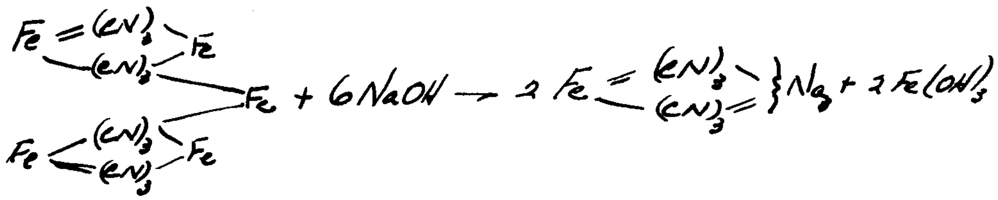
$$——(CN)_3—Fe=(CN)_3+2M^{\prime}\rightarrow—(CN)_3—\underset{M}{\underset{|}{Fe}}—\underset{M}{\underset{|}{(CN)_3}}—$$

since no part of the $-(CN)_3-\overset{(CN)_3-}{Fe}-(CN)_3-$ group is easily replaceable. The introduction of the monovalent ion into the prussian blue molecule tends to produce the maximum amount of intensity because of an increase in the number of chromophoric groups present. Hence, for the production of an intense blue a maximum amount of monovalent ion should be introduced into the molecule. Williams points out that those blue pigments which contain little $Na^{\prime}$, $K^{\prime}$, or $NH_4^{\prime}$ are not in demand by the industry, for they are not so brilliant as those containing relatively larger amounts of these same ions.

Turnbulls' Blue is closely related to Prussian Blue. The former is a ferroferricyanide while the latter is a ferriferrocyanide. The structure of Turnbulls' Blue according tó Justin-Mueller (24) is:



and treatment with sodium hydroxide produces the sodium salt of hydroferricyanic acid:



This sodium compound is red, but the iron salt is light blue.

Comparison of the two structural formulae shows a very close resemblance between them. This resemblance has been noted by Keggin and Miles (26) and Levi (33) who independently found no structural difference between sodium, potassium, or iron ferri- and ferrocyanides by X-ray examination of each. Bhattacharya (4) examined prussian blue and Turnbulls' blue by using absorption spectra and found no difference in their structures.

Briggs (10) reported the existence of two isomeric ferrocyanides of sodium and potassium, namely, a common form and a α form which may be prepared from the β by the addition of 1 % of acetic or other mineral acid to a saturated solution of the ferrocyanide. The addition of alkali or cyanide to the β will reconvert it to the α form. Locke and Edwards (34) have demonstrated the existence of two isomeric forms of the ferricyanides of potassium and sodium. The common, or α form is red while the β is a deep green. The presence of a dilute mineral acid will change the α to the β configuration. Considering the conclusions of Keggin, Miles, Levi, and Bhattacharya there may be a relationship between these four compounds although it is still open to question.

Structural Effects:

When light strikes an object, such as a pigment particle in a lacquer film, it is divided into a number of components. (See Figure 1) The pencil reflected almost unaltered from the surface B is known as "reflected" light. That passing through the particle D is designated as " transmitted " light, while C is the portion which is projected from the interior of the particle. This is designated as " pigmentary " light. The color of any pigment depends upon the innumerable selective reflections from, and transmissions through the particles. If the pigment powder presents a smooth surface it does not appear so pure in color as when rough. Loose packing permits a greater proportion of the incident light to penetrate into the body and gives color by selective reflections and transmissions B', C', D'. Therefore particle shape, size, and dispersion medium will influence the effect of incident light.

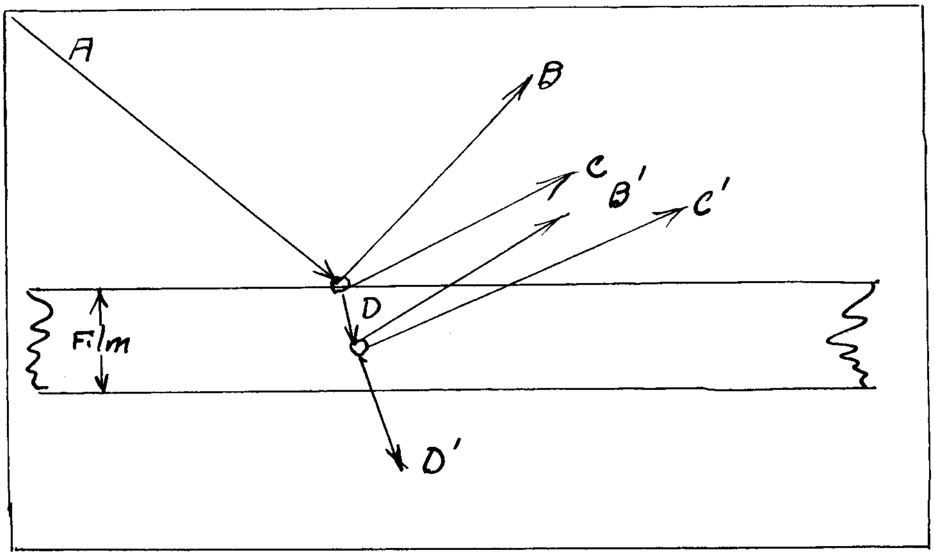


Figure 1. Path of Incident light through a Pigmented Film.

EXPERIMENTAL

For the laboratory production of the colors a general plant formula for a medium bronzed blue pigment was employed. With this formulation variables were introduced singly while all of the other values were held constant. The following steps are typical of the laboratory procedure:

Thirty-four thousandths (0.034) of a mol of ammonium sulphate ($(NH_4)_2SO_4$) was added to 0.025 mols of sodium ferrocyanide ($Na_4Fe(CN)_6 \cdot 12 H_2O$) in 500 cc of water with mechanical agitation at 60°C.

Ferrous sulphate (0.035 mols) in 200 cc of water was added slowly over a period of one half hour, during which time the temperature was maintained at 60°C and the agitation continued. When all of the ferrous sulphate ($FeSO_4 \cdot 7 H_2O$) had been added the pH was determined with an antimony electrode and digestion of the white paste continued at 60°C for another half hour.

At the conclusion of this period 0.022 mols of sulphuric acid (98 %) was added to the batch. This was followed by 0.0062 mols of sodium chlorate ($NaClO_3$) in the form of a boiling concentrated solution. Agitation was continued and the temperature maintained at 60°C during a subsequent half hour digestion. At the close of this period the pH was again taken and the pigment allowed to settle.

The pigment was washed by decantation until only traces of SO_4'' remained in the wash water. The pigment was filtered on a suction funnel and dried at 50°C in the oven. When dry the cake was ground in an agate mortar and one half gram of the finely ground material was dispersed in blown castor oil according to the method of Gardner (16).

A visual comparison was made for bronze and top-tone. The tinting strength of the sample was determined by the method of Gardner (16) and expressed as the ratio of the weights of sample to the weight of an arbitrary standard sample required to produce the same degree of tint in a definite weight of zinc white. The oil absorption of the pigment was determined according to the method of Bartell and Hershberger (20). The relative hardness of the pigment was judged by grinding the samples in an agate mortar.

The variables investigated were:

1. Temperature
    a. of the formation of the white paste intermediate,
    b. of the oxidation of the resultant intermediate paste and subsequent digestion.

2. Variation of the ammonium sulphate to sodium ferrocyanide ratio.

3. Effect of substitution for ammonium sulphate
    a. by organic nitrogenous compounds such as; aliphatic and aromatic amines, and diazonium salts,
    b. by inorganic sulphates such as $CuSO_4$, $ZnSO_4$, $MgSO_4$, $Al_2(SO_4)_3$, Li_2SO_4, $MnSO_4$, and the substitution of $Pb(C_2H_3O_2)_2$.

4. Method of Oxidation
    a. addition of the common oxidant, sodium chlorate,
    b. use of various oxidizing media,
    c. amount of oxidizing agent used per mol of sodium ferrocyanide.

5. Method of forming the intermediate white paste
    a. variation in the concentration of solutions of constituents,
    b. order of reagent addition,
    c. formation in neutral medium.

6. Variation in hydrogen ion concentration
    a. of the formation of the intermediate white paste,
    b. of the oxidation of the intermediate paste.

7. Effect of addition agents to the ferrocyanide solution
    a. sodium ferricyanide,
    b. sodium cyanide.

8. X-ray investigation.

9. Method of drying.

10. Effect of the isomeric forms of the ferrocyanides and ferricyanides on the bronzing of the pigment.

11. Particle size of various blue pigments.

12. Effect of dispersion vehicle.

13. Addition agents to the finished pigment.

14. Pigmentation in lacquer films.

DATA AND RESULTS

Temperature:

A study of the effect of temperature upon the bronzing tendencies of the pigment was made. The intermediate white pastes were formed at 0°, 25°, 45°, 60°, and 100°C, and the subsequent oxidations were carried out at 60°C in all cases. Very little variation in the amount of bronze was noted between the pigments produced, which would indicate little effect of this variable. When the temperature of oxidation was changed with the same paste forming temperature a wide variation in the red cast was noted. The change in the bronze cast caused by the variation of the oxidation temperature is shown in Figure 2. All these samples were dispersed in blown castor oil. Oxidation at the higher temperatures produced soft blue pigments. These were very high in tinting strength, relatively high in bronze hue, and low in oil absorption. Those oxidized at low temperatures produced hard, low tinting strength, and less bronzy pigments which however had an increased oil absorption. An optimum temperature for the oxidation was found to be around 25°-30°C. Oxidation at this temperature produced a blue pigment which is almost free from bronze, of medium hardness, and with a fair degree of tinting strength. The results of these runs are shown in Table I.

At temperatures above 60°C the introduction of ammonium sulphate to the original sodium ferrocyanide solution liberated ammonium cyanide (NH_4CN) and precipitated varying amounts of a dull green complex. Williams (56) discribes a material formed in the same way as ferrosoferric-ammonium-ferrocyanide:

$$Fe_2'''Fe''(NH_4)_2(Fe(CN)_6)_4$$

A sample containing appreciable amounts of the green precipitate was divided equally into two parts. The first was filtered through a double layer of filter paper on a Büchner funnel. The clear filtrate from this half was given the same treatment subsequently as the second portion which contained the complex in suspension. Samples of both final pigments were found to show the same amount of bronze.

Larger amounts of ferrosoferric-ammonium-ferrocyanide were prepared in a similar manner to that discribed previously. The complex, after drying, was dispersed with a sample of non-bronze blue in varying amounts. The resulting mixed pigment showed no increase in bronziness at any time. Dull green tones

TABLE I

Effect of Temperature Variation.

Sample number	Temp. of Paste °C	Temp. of Oxidation °C	Bronze	Tinting Strength	Oil Absorption	Hardness
16A	0	60	Bronzy	0.95	16	soft
5A	25	60	Bronzy	0.95	16	soft
IVA	45	60	Bronzy	1.00	16	soft
5B	60	60	Bronzy	1.00	18	soft
16B	100	60	Bronzy	0.95	16	soft
16C	60	0	non-bronze	0.80	22	very hard
5C	60	25	non-bronze	0.90	19	hard
IVC	60	45	slight bronze	1.00	18	medium hard
5B	60	60	bronzy	1.00	18	soft
16D	60	100	very bronzy	1.20	14	very soft

* Expressed as ratio of weight sample to weight standard to produce same tint in 5.0 grams of zinc white paste.

** Drops of blown castor oil to wet 0.5 grams of powdered pigment.

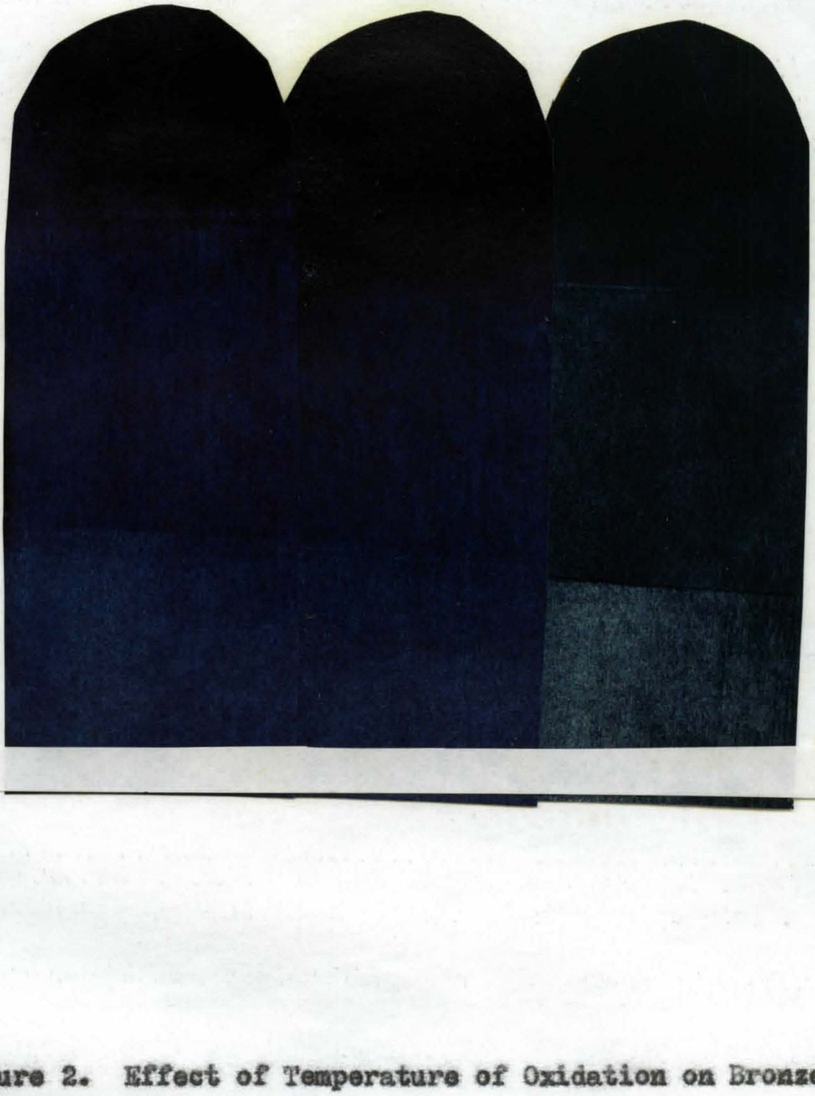


Figure 2. Effect of Temperature of Oxidation on Bronze.

were noticed when the weight of the complex was equivalent to the weight of the blue pigment used. The effect was not limited to the overtone but was also apparent throughout.

Variation of Ammonium Sulphate to Sodium Ferrocyanide Ratio:

The variation of the ammonium sulphate to sodium ferrocyanide ratio resulted in no noticeable change in the degree of bronze when the intermediate paste was oxidized at the higher temperatures. However if the mol ratio of ammonium sulphate to sodium ferrocyanide was below 1 to 2 a decrease in the tinting strength and brilliancy was noted. At the lower temperatures addition of ammonium sulphate affected the tinting strength. Non-bronze blues prepared at 25°-30°C showed a maximum tinting strength when the mol ratio of ammonium sulphate to sodium ferrocyanide was 3 to 2. If this ratio was exceeded no additional effect was noted on the pigment. (Table II) Analysis of the finished pigments prepared with varying ammonium sulphate additions to the sodium ferrocyanide showed that the amount of ammonium ion remaining in the pigment was a function of the original ratio. The graphical presentation of these data is shown in Figure 3. The ammonium content in the pigment when tinting strength was highest was found at 2.25 to 2.5 %.

TABLE II

Variation of Ammonium Sulphate Content in Formulation.

Sample number	Mols $(NH_4)_2SO_4$	Bronze	Tinting Strength	Oil Absorption	Hardness
1*	1.39	bronzy	1.00	20	soft
4*	1.39 as Mohr's salt	bronzier then 1	0.95	20	soft
5*	1.00	less bronze then 1	0.90	20	soft
6*	0.50	less bronze then 5	0.85	20	soft
20**	2.00	slight bronze	0.90	22	hard
17**	1.00	same as 20	0.95	28	hard
23**	1.39	same as 20	1.00	20	medium hard
24**	3/00	same as 20	0.85	23	hard

* Temperature held at 60°C.

** Temperature held at 25°-30°C.

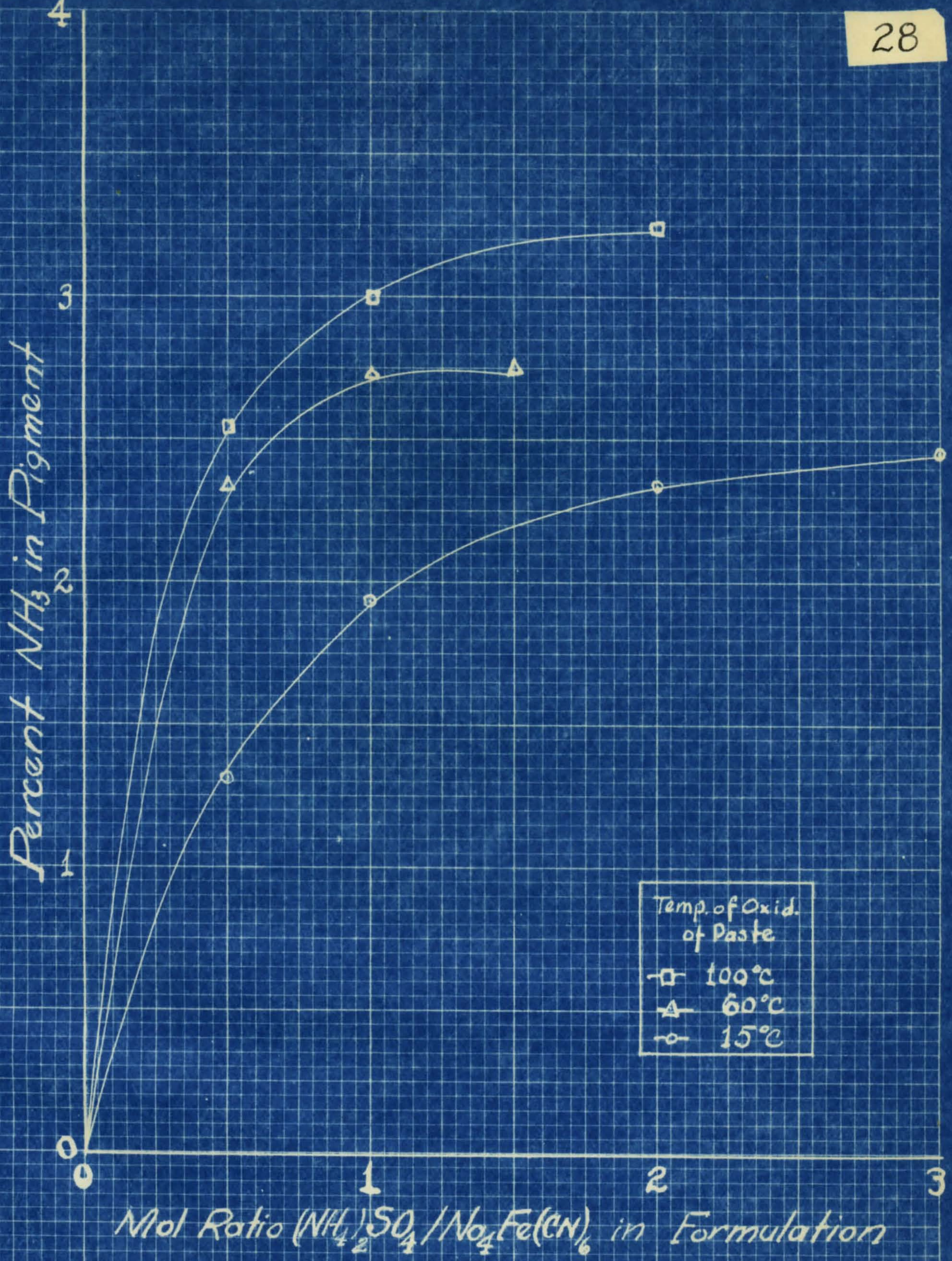


Figure 3 Ammonia Content in Final Pigment.

Pigments prepared from sodium ferrocyanide without the presence of ammonium sulphate lacked brilliancy and tinting strength, and ground very poorly in oil. It was noted that the addition of water to the oil dispersed pigment caused migration of the blue in a manner termed 'bleeding'.

As a substitute for ammonium sulphate and ferrous sulphate an equivalent amount of Mohr's salt ($Fe''(NH_4)_2(SO_4)_2$) was used. The result was comparable with the standard but showed slightly more bronze. Amines and related compounds, both aliphatic and aromatic, were substituted for the ammonium ion in an attempt to determine the effect of larger groups in the ferrocyanide molecule. In general the aliphatic groups presented a more bronzy appearance than the aromatic groups, but the bronze was in no case far different from those when ammonium was used. The outstanding difference was an apparent trend toward a green overtone. A blue pigment made in the presence of urea was exceptional in this respect. (Table II) (Figure 4).

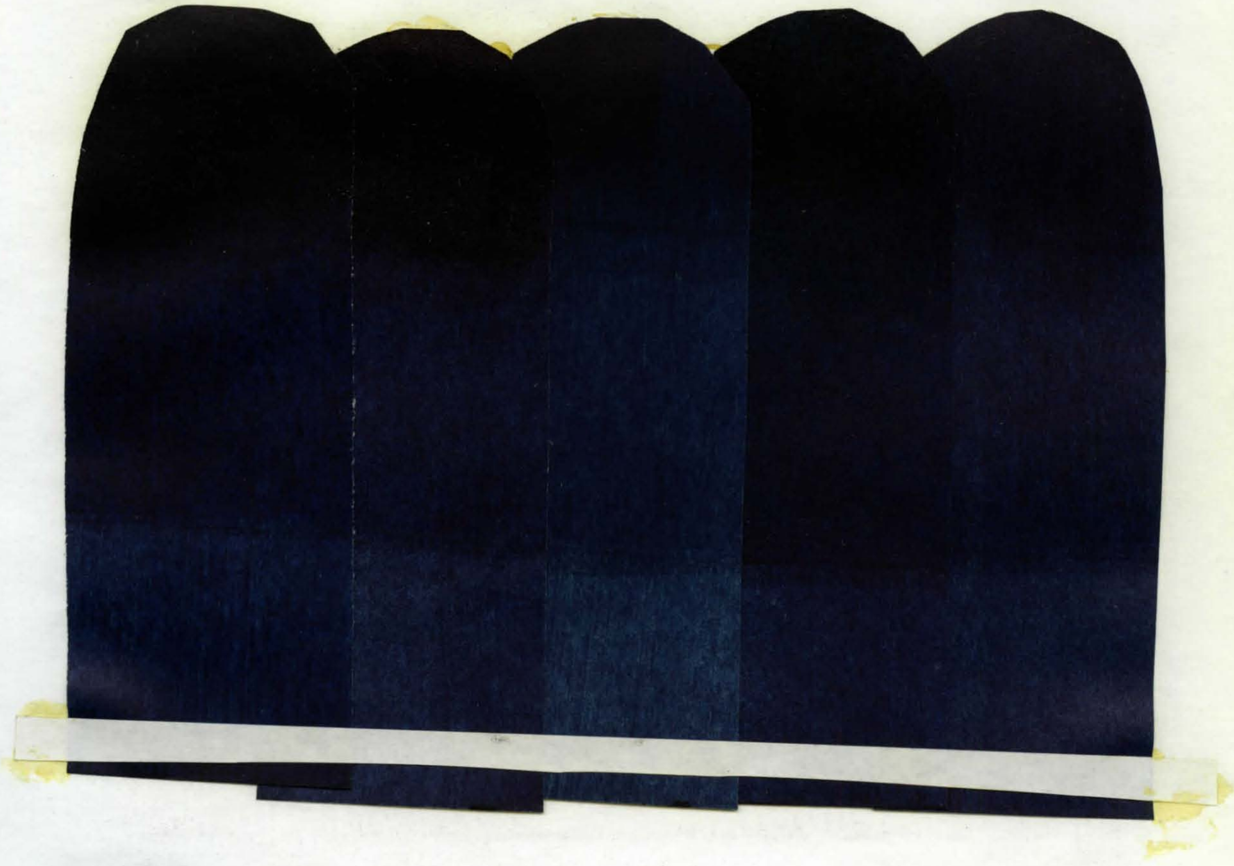
In one experiment toluidine was diazotized and the diazonium chloride was made to react with sodium ferrocyanide. Ferrous sulphate was added and the paste oxidized in the usual manner. The pigment was green-yellow in color and did not re-

TABLE III

Effect of Addition of Organic Amines in Place of Ammonium Sulphate.

Sample number	Amine	Mol ratio Amine to $Na_4Fe(CN)_6$	Bronze	Tinting Strength	Oil Absorption
7*	dimethyl aniline	1.39	medium bronze	0.90	15
8	diphenyl amine	1.39	less then 7	0.90	15
9	urea	1.39	non-bronze green top-tone	0.80	18
10	triethanol amine	1.39	more bronze then 7	0.85	14
10B	Methyl-ethyl amine	1.39	bronziest	0.95	14
10C	diethanol amine	1.39	less bronze then 10B	0.95	15
7B	aniline	1.39	more bronze then 7	0.95	15
10D	pyridine	1.39	similar to 10C	1.00	15
DB	p-methyl phenylazonium chloride	1.39	green-yellow	--	10

* Temperature held constant at 45°C throughout.



Ammonium sulphate
dimethyl aniline
diphenyl amine
urea
triethanol amine

Figure 4. Replacement of Ammonium Sulphate by Organic Amines.

semble the prussian blue pigments. Extraction of this pigment with various solvents did not discharge the color; therefore it was assumed that the toluidine was in combination with the ferrocyanide.

When aluminum, copper, zinc, lead, and arsenic salts were used in place of the ammonium sulphate the pigments were discolored, muddy, low in tinting strength, and still showed the bronze cast. When lithium sulphate was used a fine color was produced which resembled that made from potassium ferrocyanide. (Table IV) (Figure 5).

Method of Oxidation:

The oxidation of the white paste was accomplished under various conditions.

1. Using sodium chlorate ($NaClO_3$), which is the commonly used oxidant, the method of addition was varied from the crystalline solid to a dilute solution slowly added with vigorous mechanical agitation. The former showed considerably more bronze ther the latter. (Table V)

2. The relative amount of sodium chlorate used was varied between the ratio of sodium chlorate to sodium ferrocyanide 0.1 to 1 and 1.25 to 1, but the useful range for the production of prussian blues fell between 0.20 to 1 and 1 to 1.

TABLE IV

Effect of Substitution of Inorganic Salts for Ammonium Sulphate

Sample number	Compound	Mol ratio per mol $Na_4Fe(CN)_6$	Bronze	Tinting Strength	Oil Absorption
11*	$Al_2(SO_4)_3$	1.39	bronze	0.70	25
12	$CuSO_4$	1.39	green	0.40	23
13	$ZnSO_4$	1.39	very bronze	0.85	21
14	$Pb(C_2H_3O_2)_2$	1.39	jet	0.60	20
15**	$CuSO_4$	1.39	bronze	0.50	23
19	$ZnSO_4$	0.25	bronziest	0.90	20
43	$MnSO_4$	1.39	brown	0.80	20
40	Li_2SO_4	1.39	very bronze	1.10	18
44	Na_2AsO_4	1.39	green	0.80	22

* Temperature held constant at 60°C throughout.

** Unoxidized.

Figure 5. Effect of Replacement of Ammonium Sulphate by Inorganic Salts.

TABLE V

Method of Addition of the Oxidizing Agent.

Sample Number	Method of Addition of $NaClO_3$	Bronze	Tinting Strength	Oil Absorption
29*	solid	very bronzy	1.05	19
30	hot concentrated soln.	bronzy	1.00	19
31	hot dilute soln.	less than 30	1.00	20
32	cold dilute soln.	less than 31	1.00	20

---

* Temperature held at 45°-50° throughout.

Below the lower value the oxidation was not sufficiently complete to produce a satisfactory color, and above the upper value a soluble blue was formed. The bronze cast increased as the ratio became larger. In one case where the ratio was 0.976 to 1 a definite redness developed while the pigment was still in suspension, the material was colloidal and could not be filtered. A portion of this pigment suspension was concentrated by evaporation and the water removed by alcoholic washings which were followed by an ether wash. After drying this residue and dispersing it in oil it showed extreme brilliancy, a very high tinting strength and the maximum amount of redness found in the entire investigation. The light reflected from the surface of the test specimen showed a purple-red, yet the top-tone and the tints of the pigment in zinc-white appeared blue and lost almost all the bronze cast. This pigment was also incorporated in a lacquer, and a series of films of varying thickness were cast. Examination of these showed that with transmitted light a blue color was seen when viewed normal to the film. A glancing pencil of light produced a purple-red shade. The red coloration became more apparent as the intensity of the light source was increased. Under a carbon arc the blue is almost lost in the light reflected from the pigment particles, and the color of the specimen under these conditions approaches a deep red. (Table VI)

3. The oxidation was investigated with the use of potassium dichromate ($K_2Cr_2O_7$), potassium permanganate ($KMnO_4$), nitric acid, air, hydrogen peroxide, sodium hypochlorite, ($NaOCl$), ferric nitrate ($Fe(NO_3)_3$), and perchloric acid ($HClO_4$). In order to reduce the various oxidants to a common basis for comparison, 0.525 oxygen equivalents were taken for each mol of sodium ferrocyanide. The results are tabulated in Table VII. The rapid addition of potassium dichromate caused a green undertone to appear, especially if the oxidation were conducted at temperatures above 60°C. The bichromate produced the bronziest blue pigments. The use of permanganate produced blue pigments which were jet in top-tone, black in the dry state and were all characterized by a green under-tone. The blues prepared by using sodium hypochlorite varied in the degree of bronze even with duplicate formulations. Air oxidation was slow and required 8 to 10 hours. The pigment was weak and did not have any lustre. The use of nitric acid produced green top-tones

TABLE VI

Effect of Concentration of Oxidizing Agent.

Sample Number	Mol ration $NaClO_3$ to $Na_4Fe(CN)_6$	Bronze	Tinting Strength	Oil Absorption
25*	0.976	bronziest	0.95	17
26	0.732	less than 25	0.95	19
24	0.244	least bronze	1.00	20
28	0.122	light blue due to insufficient oxidation.		

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* Temperature held constant at 15°C.

TABLE VII

Effect of Various Oxidizing Agents.

Sample Number	Oxidant	Mols O_2 equivalent per mol $Na_4Fe(CN)_6$	Bronze	Tinting Strength	Oil Absorption
LB1A*	$K_2Cr_2O_7$	0.244	bronziest	1.10	17
LB1B	H_2O_2	0.244	less then LB1E	0.95	21
LB1C	$KMnO_4$	0.244	bronze jet top-tone	1.00	20
LB1D	HNO_3	0.244	bronze green top-tone	0.95	21
LB1E	$NaClO_3$	0.244	bronze	1.00	20
LB1F	Air	-------	least bronze	0.85	22
LB1G	$Fe_2(SO_4)_3$	0.244	less then LB1E	0.90	19
LB1H	$HClO_4$	0.244	bronze	1.00	20

* Temperature held at 30°C.

around 80°C could be made to produce a green pigment by excess addition. The paste which was oxidized with perchloric acid made a blue comparable to that using sodium chlorate. The use of ferric sulphate resulted in a pigment with a brown top-tone, and when incorporated in tints showed a grey discoloration. The results of oxidation with hydrogen peroxide were comparable to those obtained with sodium chlorate.

Electrolytic oxidation was tried, but there was no appreciable decrease in the bronze tone. When the oxidation was buffered with urea, fructose, and benzaldehyde very little variation in bronze was noted.

Concentration of Solutions:

The concentrations of the sodium ferrocyanide and the ferrous sulphate were varied, and the dilute solutions produced the brightest blues, but little effect was noted on the bronze cast. An optimum concentration was found at about 2.5 % sodium ferrocyanide solution and 10 % ferrous sulphate solution. Very concentrated solutions of either ferrous sulphate or ferrocyanide produced brown top-tones and dull shades of blue with a decrease in the bronze. (Table VIII)

TABLE VIII

Effect of Concentration of Sodium Ferrocyanide and Ferrous Sulphate Solutions.

Sample Number	Concentration $Na_4Fe(CN)_6$	$FeSO_4$	Bronze	Tinting Strength	Oil Absorption
A*	100 cc	100 cc	non-bronze	0.95	20
B	50 cc	50 cc	brown top-tone	0.95	19
C	400 cc	400 cc	slight bronze	1.00	19
D	500 cc	200 cc	bronze	1.05	20
E**	500 cc	500 cc	bronze	1.30	17
F**	500 cc	200 cc	bronze	1.30	17

* Temperature held at 25°-30°C.
** Struck in neutral medium.

A brighter blue may be obtained at the higher temperatures when ammonium sulphate is added to the ferrous sulphate solution. This addition also prevents the formation of the ferrosoferric-ammonium-ferrocyanide complex previously mentioned. Less bronze was produced when the sodium ferrocyanide was added to the ferrous sulphate. Moreover, if the pH were around 5.5 after oxidation there appeared a brown coloration in the finished pigment. The results indicate that a blue should be struck in neutral medium with the ferrous sulphate addition slightly ahead of the ferrocyanide at all times. A temperature of 25°-30°C with the above procedure produced an almost non-bronze blue of high tinting strength and medium softness. (Table IX)

Hydrogen Ion Concentration:

The formation of the intermediate white paste was carried out at various hydrogen ion concentrations. At very low pH values the paste was more gelatinous and and colored, while formation at a pH of 5.5 produced a granular paste which settled rapidly and was nearly white. Oxidations performed at a pH below 4.0 resulted in bright, soft, brilliant blues which were rather bronzy. When the

TABLE IX

Sequence of Addition of Reactants for the Formation of the Intermediate Paste.

Sample Number	Method of Addition of Reactants	Bronze	Tinting Strength	Oil Absorption
J*	ferrocyanide to ammonium sulphate and ferrous sulphate	slight bronze	0.85	18
JI	ferrous sulphate to ferrocyanide and ammonium sulphate	bronze	1.00	20
JII	neutral medium	more bronze than JI	1.15	17
JIII	neutral medium ammonium sulphate to the ferrous sulphate	bronze	1.05	20

* Temperature held at 45°C.

pH of oxidation was 5 the pigment was found to be very much decreased in bronze, easily washed and filtered. The neutralization of the paste previous to oxidation and a subsequent oxidation at a pH of 7 resulted in a product which could not be filtered. (Table X)

Effect of Addition Agents to the Ferrocyanide:

The addition of small amounts of sodium cyanide to the ferrocyanide resulted in a more bronzy pigment in every case (Table XI). This same trend was noted when sodium ferricyanide was added to the ferrocyanide. Progressive additions of the ferricyanide made suspended pigments which were harder to filter as well as making an increasingly bronzy blue. (Table XII) The wash water which was decanted from these blues was characterized by a pronounced redness even after as many as ten (10) successive washings. In no case did this coloration wash out completely. The addition of small amounts of ferricyanide (0.025 molar) showed only faint traces of this coloration in the wash water, but the pigment was very finely divided.

The addition of 0.1 % of potassium alum to the ferrocyanide was found to act as a color intensifier and

TABLE X

Effect of pH on Oxidation and Paste Formation.

Sample Number	pH of Paste	pH of Oxidation	Bronze	Tinting Strength	Oil Absorption
21*	6.0	4.45	jet non-bronze	0.90	20
22	6.0	5.00	non-bronze brown tone	0.90	20
23	6.0	2.10	bronze	0.95	20
24	6.0	1.30	bronze	1.00	18
21A	4.0	2.30	very bronze	1.05	18
45	2.1	1.10	bronziest	1.10	17
22A	6.0	5.50**	non-bronze brown tone	0.90	21

* Temperature held at 25°-30°C.

** NaOH added prior to digestion until pH was 5.5

TABLE XI

Effect of Addition of Sodium Cyanide to the Ferrocyanide.

Sample Number	Mols NaCN	Bronze	Tinting Strength	Oil Absorption	Hardness
ADS8*	0.025	bronzy	1.05	18	soft
ADS9	0.005	less than ADS8	1.00	19	soft
ADS10	------	non-bronze	1.00	19	soft

* Temperature held at 30°C.

TABLE XII

Effect of Addition of Sodium Ferricyanide to the Ferrocyanide.

Sample Number *	Mols $Na_3Fe(CN)_6$	Mols $Na_4Fe(CN)_6$	Bronze	Tinting Strength	Oil Absorption
ADS1*	0.50	0.50	more bronze than ADS2	1.10	18
ADS2	0.25	0.75	least bronze	1.15	18
ADS3	0.75	0.25	more bronze than ADS1	1.10	17
ADS4	1.00	1.00	bronziest	0.85	15

* Temperature held at 60°C.

and totally removed the brown top-tones which were usually produced at a pH over 6. Amounts of potassium alum above 0.1 % of the ferrocyanide were found to produce weaker colors which lacked brilliancy.

X-Ray Investigation:

An x-ray comparison of a highly bronzed and a non-bronze blue failed to reveal any structural differences between the two. A spectroscopic analysis showed the presence of similar impurities in each blue, notably 0.001 - 0.01 % Al, 0.001 - 0.01 % Mn, and 0.001 - 0.1 % Cr.*

Method of Drying:

Pigments which were dried in an oven above 70°C all showed ugly red casts. They were hard to grind and a dispersion in an oil was very difficult to produce because of the low wetability. However if these pigments were not sufficiently dispersed they presented a jet top-tone with practically no tinting power. At lower drying temperatures a similar effect was noticed when a low humidity drying atmosphere was employed. Pigments with the most desireable properties were obtained when dried at 65°C in an atmosphere

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* Private communication from the Dow Chemical Co., Midland, Michigan.

with a relative humidity of 50 % or above. The results of various drying temperatures are shown in Table XIII.

Isomeric Forms:

The isomeric forms of the ferrocyanides were prepared by the method of Briggs (10) and the α and β forms separately made into pigments under similar conditions. There was no appreciable variation in the degree of bronze when the draw-downs of the pigments were compared.

Particle Size:

A dry blue pigment which showed a fair amount of bronze was shaken with ethyl acetate for thirty minutes in a separatory funnel and then allowed to settle. Periodically the settled particles were removed and dried, and subsequently rubbed up in blown castor oil. The slower settling fractions showed decidedly greater amounts of bronze. Three fractions are shown in Figure 6. The times of settling were in the ratio of 1 to 12 to 48. The tinting strength of the pigment varied directly with the bronze.(Table XIV)

A non-bronze blue pigment suspension in water was refluxed for varying lengths of time. Eight (8) hours was sufficient to produce appreciable peptization which pro-

TABLE XIII

Effect of Drying on the Bronzing of the Blue.

Sample Number	Drying Temp. °C	Relative Humidity	Bronze	Tinting Strength	Oil Absorption
LB	105	oven	jet	0.75	28
LB	85	oven	slight bronze	0.85	24
LB	70	20	bronze	0.90	23
LB	100	50	jet	0.80	26
LB	65	50	slight bronze	1.00	20
LB	50	10	bronze	1.05	19

TABLE XIV

Effect of Particle Size on Bronze and Tinting Strength.

Fraction *	Tinting Strength	Bronze	Oil Absorption	Hardness
fastest settling	0.95	bronze	20	soft
medium fast settling	1.00	more than above	19	soft
slowest settling	1.00	more than middle fraction	18	very soft
residue on evaporation	0.80	bronziest	16	very soft

* Settled in ethyl acetate.

largest medium smallest

Figure 6. Effect of Particle Size on Bronze in Blown Castor Oil.

gressed to completion and the bronze tint of the material increased proportionately. At the point of complete peptization the suspended material in the liquid was a deep purple color. Samples evaporated from the mixture at varying times showed a tinting strength increasing to a maximum shortly before complete peptization was produced. (Table XV)

Dispersion Vehicle:

It was found that various pigment vehicles caused the sample pigment to assume varying degrees of bronze. This phenomenon is shown in Figure 7. When the test sample had dried, a thin coat of clear lacquer applied to the surface decreased the bronze. (Figure 8)

Addition Agents to the Finished Pigment:

A sample of the pigment which showed exceedingly large amounts of the bronze was mixed and dispersed with various types of black pigments and the results noted on the mixed draw-downs. In some cases the bronze was decreased until it was not perceptible, yet the color of the mixed pigment still appeared blue. Of all the additive blacks which were tried, Ivory Black was found to be the most

TABLE XV

Effects of Thermoageing on the Bronze and Tinting Strength of a Pigment.

Time of Reflux in Hours	Bronze	Tinting Strength	Oil Absorption	Hardness
0.0	medium bronze	1.00	20	medium hard
0.5	medium bronze	1.05	20	medium hard
1.5	bronze	1.10	20	soft
4.0	increasingly bronze	1.10	20	soft
6.0	very bronze	0.95	19	very soft
8.0*	most bronze	0.80	16	very soft

* Pigment recovered by evaporation.

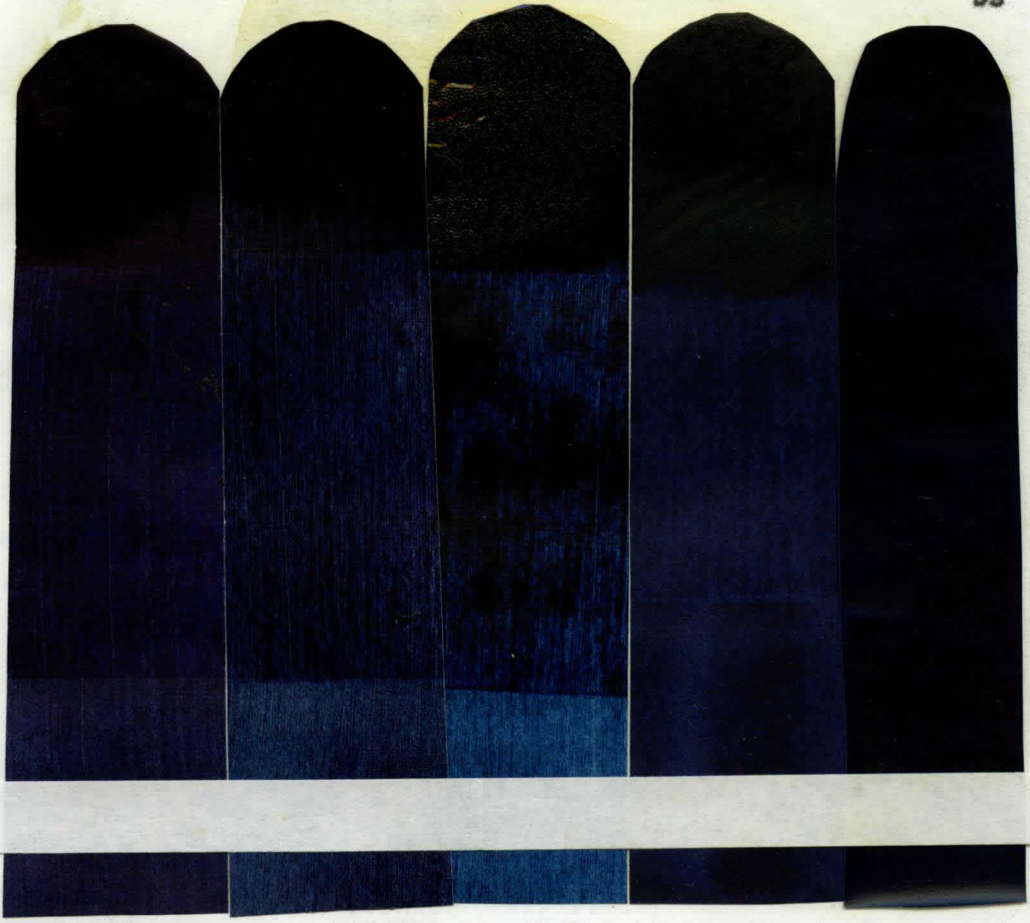
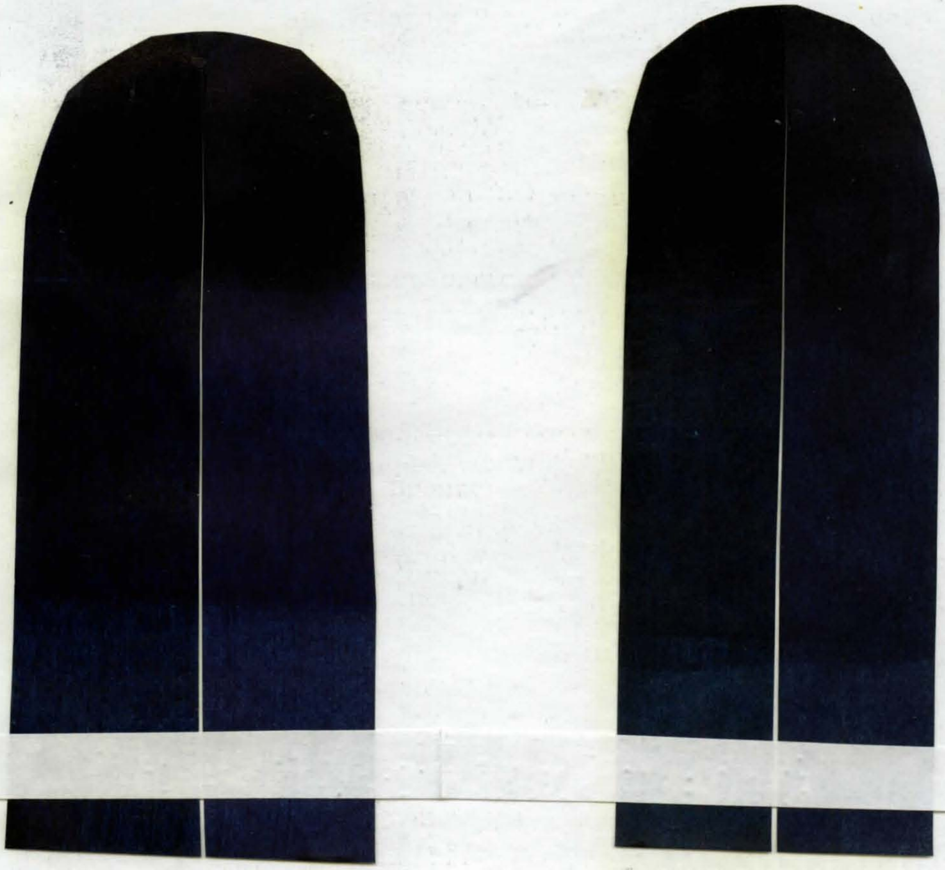


Figure 7. Effect of Pigment Vehicle on the Bronze.



coated uncoated
blown castor oil.

coated uncoated
lithol varnish.

Figure 8. The Effect of Coating the Dry Film with Lacquer.

suitable while Carbon Black resulted in red-brown tints.

Pigmentation in Lacquer Films:

The various blues were incorporated in lacquers having the same base formula. Later they were drawn out into films on a glass plate and removed after a drying period of one week. An examination of the film for the bronze cast showed its presence when both the top and underside of the film were illuminated by incident light. In some cases the bronze evident on the underside was even more pronounced than that of the top side. Normal transmitted light showed a nearly true blue color but glancing transmitted light produced a near purple shade.(Figure 9)

Simultaneous incorporation of blacks in the blue pigment - lacquer grind resulted in a decrease in both bronze and total incident reflected light. The effect on transmitted light was similar.

Figure 9. Pigmented Lacquer Films.

DISCUSSION OF RESULTS

A study of the results reported in the previous section reveal that the factors which seem to contribute to the bronze in the prussian blue pigments were as follows:

1. Oxidation of the intermediate white paste at high temperatures,
2. Oxidation of the intermediate paste at low pH values,
3. The addition of the oxidizing agent in the form of a concentrated solution or as a solid,
4. An excess of sodium chlorate,
5. The use of strong oxidizing agents,
6. Low concentrations of ferrous sulphate and sodium ferrocyanide solutions,
7. The addition of the ferrous sulphate to the sodium ferrocyanide,
8. The addition of sodium ferricyanide and sodium cyanide to the original solutions,
9. Reduced particle size (obtained by sedimentation separations),
10. Peptization of the pigment through thermoageing,
11. Low refractive index of dispersion vehicle.

The examination of these factors contributing to a more bronzy blue pigment indicated the similarity of all but one, in that they result in a decreased particle size. The average particle size can be considered as a function of the particle size distribution and this may be affected in two ways, first, a peptizing influence on the pigment, and second, by the formation of microcrystalline nuclei which are inhibited in growth. The latter results in the formation of finely divided particles of approximately uniform size while the former would tend to give a wide distribution of size. Finely divided pigments show a brilliancy of color, high tinting strength, ease of grinding, and dispersion in oil.

Physico-chemical laws indicate that crystal formation should take place more rapidly at high temperatures and in highly acid solutions, conversely at low temperatures and higher pH values the crystalline formation would be slow. Digestion at high temperature of a curdy blue pigment which was formed by oxidation of a gelatinous white paste causes the formation of small crystalline nuclei whose growth is inhibited by the presence of various ions. A general result similar to this has been reported by Wooller (58).

The addition of a concentrated oxidizing agent results in a localized saturation of the solution with the oxidant and may exert a peptizing influence on the resultant blue pigment. Bunagh (12) reports that prussian blue pigments may easily be peptized by the use of potassium dichromate, and we have no reason to believe that this is the only oxidant to affect pigments in this manner. The effect of negatively charged ions on the coagulation of prussian blue has been reported by Ghosh and Dahr (61), whose findings are in accord with those above.

A localized concentration of oxidant in the batch may also carry the oxidation of the paste to the secondary stage, that is, oxidation of the ferro- to the ferricyanide. The formation of the ferricyanide greatly aids the hydrolysis of the ferriferrocyanide with the formation of the stabilizing ferrocyanide ion. The ferricyanide itself may act as a stabilizing ion for the prussian blue sol. This is in agreement with the works of Ghosh and Dahr (61) and Wooller (58). After the formation of ferricyanides where the oxidant has been most concentrated, mechanical agitation would cause the ferricyanides to come in contact with some of the unoxidized paste intermediate. The result would be an oxidation of the paste to prussian blue and the reduction of the ferricyanide to more of the ferrocyanide. As the oxidation-reduction proceeds it would slowly reach an equilibrum, and there would still be some ferricyanide in the presence of the ferrocyanide. The kinetics of this electron movement from ferri- to ferrocyanide are such that crystalline growth of the blue pigment would be inhibited and the stabilizing action on the colloid would result in a finely divided pigment.

The identification of ferricyanide in the final blue is difficult for a number of reasons. The crystal structure of both ferro- and ferricyanides are similar and the x-ray has been unable to produce a means of detection of one in the presence of the other. Chemical methods of identification are not effective, since during the analysis the pigment is boiled with a potassium hydroxide solution which would cause the reduction of ferricyanide by either the adsorbed ferrous ammonium sulphate, the ferroammonium-ferrocyanide, or both. This makes the identification of very small amounts of ferricyanide improbable under these conditions.

The presence of ferricyanide and cyanide were studied by the addition of known amounts of each to the ferrocyanide. This added to the evidence for the concept of peptization and stabilization of the resultant colloid.

The presence of excess sodium chlorate and other strong oxidizing agents afforded similar results. Nitric acid and sodium hypochlorite produced green top-tones and at first seems to be an exception to this supposed mechanism, but the investigations of Ghosh and Dahr (62) afford an explanation. Their work reports that only small quantities of potassium chloride and potassium nitrate are required to coagulate prussian blue when in the presence of hydrochloric or nitric acid. He proposes a decrease in the hydrolysis of prussian blue with the corresponding decrease of the stabilizing ferrocyanide ion. This would produce a larger particle size. Astington and Hancock (2) studied the effect of various oxidizing media and found that the yield of pigment was lowest for severe oxidations with potassium chlorate in acid solution while that oxidized with ferric sulphate in acid solution was highest. Yield may be taken as a measure of relative fineness of a pigment provided the adsorption is not excessive, for the finely divided pigments the loss in washing is greatest.

The formation of the pigment in dilute solution enables the gelatinous blue material, first formed by the oxidation of the intermediate paste, to rearrange itself into finely divided microcrystalline nuclei which produce finely divided pigments. Total ionic concentration exerts a marked effect on the growth of the prussian blue particle after oxidation as well as on the precipitation of the resultant pigment. The work of Weiser and Nicholas (54) infers the formation of finely divided pigments in dilute solutions of ferrous sulphate and ferrocyanide.

The work of Joshi and Singh (23) indicates that thermoageing of prussian blue pigments will in most cases produce an increase in the viscosity of the oil-pigment mix as well as decrease the transparency. An increase in viscosity indicates a fine dispersion of the pigment in the oil while a decrease in transparency shows greater tinting strength which in almost all cases is associated with small particle size.

The addition of the ferrocyanide to the ferrous sulphate solution results in a white paste which produces a coarse grained pigment, but if the ferrous sulphate is added to the ferrocyanide the unreacted ferrocyanide exerts a peptizing action on the intermediate paste. The first produces a granular paste because of the ferrous ion present during the entire formation period, but the latter results only in coagulation after there is an excess of ferrous sulphate. This coagulation is not so complete as in the first case, and a smaller average particle size will result.

The average particle size of a prussian blue makes it impossible to use the microscope for a particle size determination and the sedimentation method of Kelly (27) is also open to question. Objections to the latter are due to the length of time of settling of the pigment and the error introduced by evaporation over this period. The method of settling, however, affords a qualitative relationship by which particle size and bronzing characteristics in the pigment may be correlated. Pigments settling at different rates would contain a different average particle size and were readily compared for bronze and tinting strength. It will be noted that these results support the particle size-bronze relationship.

Drying of prussian blue may be considered as a process of removal of water between the pigment particles and the resultant agglomeration or grouping of these particles into lumps. Conditions of drying which tend to result in case-hardening produce pigments difficult to grind in oil and lack tinting strength. These case-hardened pigments show a high intensity of reflected light prior to and after grinding, and a small percent of incident light which is reflected only slightly changed in spectral character produces an ugly red cast. When the moisture is slowly removed the pigment ske is porous and easily ground and dispersed in oil. The incident light is able to penetrate deeply into this type of pigment surface and as a result very little light is reflected. This pigment appears a rich blue.

The relationship between particle size and bronziness of the blue may be deduced from optical considerations. When a pigment of this nature is dispersed in a medium it is essentially a colloidal system and will follow most of the laws governing colloids (3)(20)(42). Radiant energy is regularly reflected from the surfaces of the pigment particles. Should the pigment surfaces be properly oriented, this light will return to the eye unchanged in spectral character. The reflection-factor of black pigments varies from 0.02 to 0.1. This variation causes the appearance of black pigments to vary between a bluish and a red tone. (35)

The particle size distribution in the prussian blue covers a wide range between those close to molecular dimensions to those visible by the naked eye. The particles whose diameter is close to or less than the wavelength of light exert a marked influence toward a bronze hue. The wave front of light scattered by an object which is smaller than the wavelength of light itself will be spherical, regardless of the shape of the particle since there can be no interference between waves emmited by the several points. The intensity of the scattered light in this case would be proportional to the reciprocal of the wavelength raised to the fourth power (22). i.e.

$$I = K \frac{1}{L^4} \quad \text{(Rayleigh Equation)}$$

where I is the intensity of the scattered light,
L is the wavelength of the light,
K is a proportionality constant.

Consider a pencil of incident light consisting of equal intensities of red and violet of wavelengths 7200 and 4000 respectively. This beam could be scattered by a particle smaller than the wavelength of either. Then the ratio of the intensities of the scattered light would be:

$$\frac{I_r}{I_v} = \frac{K \frac{1}{(7200)^4}}{K \frac{1}{(4000)^4}} = \frac{1}{10}.$$

or the intensity of the red unscattered light would be ten times that of the violet from a particle smaller than the wavelength of either, and the system will appear to have a red cast.

Luckiesh (35) refers to the relationship between pigments and their vehicles as follows:

> ' Most vehicles when dried have refractive indices in the neighborhood of 1.5 and this indicates that the amount of light regularly reflected from the smooth surface of the vehicle is about 4 percent. A substance to be most effective as a pigment should have a high refractive index for the hue it most freely transmits. The refractive index varies considerably in the neighborhood of an adsorption band, being greater on the long-wave side than on the short-wave side. This is the reason for the greater refractive indices usually exhibited by yellow, orange, and red pigments than by blue and violet. If the refractive index of a pigment closely matches that of the vehicle, the former will diffuse very little light. Such a pigment would ordinarily be mixed with one of higher refractive index which will diffuse the light. '

This would indicate that for a purity of color the grains should be uniform, and that there should be no selective scattering of light by the pigment or vehicle. The results of this investigation bear out this principle by indicating a change in the bronze tone of a pigment dependent upon both the average particle size and the vehicle employed. Higher refractive indices produced lowest apparent bronze.

In many cases the degree of bronze of a pigment will increase with the age of the film. This may be caused by the slow evaporation of the solvent which tends to carry the sub-microscopic particles to the surface of the film where they become more effective in scattering the light. Furthermore, as the smooth film wears away, more light is reflected from the small particles themselves than from the original film surface. The result would be a greater scattering effect because of the small particles. Analogous phenomena have been noted by Bancroft (3) in the study of natural pigmentations.

Examination of the factors affecting the tinting strength of the pigment reveal a decrease in tinting strength as follows:

1. Ammonium sulphate in excess to 1.5 mols per mol of sodium ferrocyanide,
2. Presence of adsorption products or admixture of decomposition products in the paste,
3. Ammonium sulphate lower than 0.5 mol per mol of sodium ferrocyanide,
4. Coarse particle size,
5. Colloidal particle size.

These factors may be grouped as bringing about the decrease in tinting strength in three ways:

1. by the adsorption or admixture of a material which acts as a diluent in the pigment,

2. by a variation in molecular constitution produced by chemical constituents,

3. by the lack of proper dispersion of the pigment in the vehicle.

During the formation of the intermediate white paste and thereafter the phenomena of adsorption and occlusion readily take place because of the gelatinous nature of the material. A quantity of all the materials present in the surrounding liquors will therefore be present to some extent in the finished pigment. In a general way it can be stated that adsorption will be greatest for materials of similar composition and structure and that a less soluble material will be adsorbed to a larger extent than a more soluble material. Factors such as temperature of precipitation, temperature of digestion, amount of dilution, rate of agitation, pH value, method of washing the precipitate, rate of addition of reagents, and the amount of reagents added affect the degree of adsorption attained.

Increased amounts of ammonium sulphate per mol of ferrocyanide above a ratio of 3 to 2 result in an increased adsorption and occlusion in the finished pigment. The curves (Figure 3) are indicative of adsorption since we would expect well defined steps if a definite compound was formed. The adsorption of sodium ferrocyanide in prussian blue has been demonstrated by Thrus (21). This phenomena is also true of sodium ammonium ferrocyanide ($Na_3(NH_4)Fe(CN)_6$) which is readily formed when the ammonium sulphate is added to the sodium ferrocyanide. The solubility of this mixed salt is decreased in the presence of other salts (56) and adsorption is favored. This mechanism of adsorption seems a more logical one than the mere occlusion or adsorption of sodium ferrocyanide which is readily soluble in water. On oxidation these double salts form the corresponding ferricyanides (32)(44)(56). A list of the compounds which may be present in the liquors following oxidation is shown in Table XVI.

Increased adsorption of sodium ferricyanide may lead to 'bleeding' characteristics in the pigment for it is deliquescent and more easily wet by water than by oil.

TABLE XVI

Compounds Present During the Formation of Prussian Blue.

Compound	Color	Crystalline Structure
$Na_3Fe(CN)_6$	red	deliquescent
$(NH_4)_3Fe(CN)_6$	red	crystalline
$(NH_4)_2NaFe(CN)_6$	red	crystalline
$Fe_2(SO_4)_3$	tan	deliquescent
$Fe(OH)(SO_4)_2$	brown	amorphous
$Fe(OH)_3$	red-brown	amorphous

The adsorption of compounds which are red would lead to a discoloration in the pigment which would be primarily evident by transmitted light. This discoloration of the pigment would tend to decrease the tinting strength.

The presence of ammonium sulphate below the ratio of one mol per two mols of ferrocyanide results in the formation of a coarse granular pigment, low in tinting strength. This decrease in tinting strength can be understood best after a brief survey of the chemistry of the potassium, ammonium, and sodium salts of ferrocyanide. When ammonium or potassium ferrocyanide is precipitated by an excess of ferric salt, a blue compound of the formula $Fe'''M'Fe(CN)_6 \cdot X\ H_2O$ is obtained (56) where M' is either NH_4' or K' and X is eight or ten. No compound corresponding to this formula with sodium has as yet been prepared (56). The mixed salt is more brilliant and contains less water of hydration than any of the double salts of ferriferrocyanide and sodium ferrocyanide ($Fe_4(Fe(CN)_6)_3 \cdot X\ H_2O \cdot X'\ Na_4Fe(CN)_6$). The latter usually contains as many as one hundred molecules of water of hydration (56). Added water as well as the formation of the double salt appears instrumental in lowering the tinting strength and the color intensity of the chromophoric groups in the molecule.

The introduction of bi- and trivalent ions in the prussian blue molecule similarly to the introduction of ammonia or potassium appears improbable, and although mixed salts with bi- and trivalent ions are reported (56), there is still some question as to their possible structure.

The presence of coarse particles of pigment in a vehicle tends to decrease the surface volume of the blue and thus tends toward a lowered tinting strength. In every case where the dispersion of the pigment in oil is poor the ratio of the surface volume of pigment to the surface volume of the zinc white will be decreased and the blue will not appear as strong in color. The pigments made solely from sodium ferrocyanide were all coarse in structure and attempts at dispersion resulted in fairly large granular particles with low tinting strength and green tone characterized by the absence of bronze. Moreover pigments which were on the verge of being peptized showed a low tinting strength. Between these two extremes the tinting strength reached a maximum, but the bronze increased continually.

This phenomenon is not uncommon with pigments and has been observed by Wooller (58) and Luckeich (35). The latter attributes the final decrease in tinting strength of the pigment to the reduction in particle size. Particles smaller in size than the wavelength of light require a greater depth to absorb the required amount of light from the incident beam before the sensation of color is produced.

SUMMARY

It was found that an increase in the temperature of oxidation of the intermediate paste produced higher bronze in the pigments. An optimum temperature for a non-bronze blue was found at 25°-30°C.

The presence of complex decomposition products did not affect the bronzing tendencies of the pigment but were instrumental in decreasing the tinting strength.

A variation of ammonium sulphate content did not appreciably affect the bronze, but between molal ratios of 0.5 - 1.5 per mol of sodium ferrocyanide produced pigments high in tinting strength and intensity.

Complete absence of ammonium sulphate produced a granular blue pigment, green in top-tone, low in tinting strength and brilliancy, and preferentially wet by water.

Replacement of ammonium sulphate by inorganic salts resulted in a lowered tinting strength and brilliancy, while the organic replacements produced pigments comparable to those made with ammonium sulphate. The substitution of lithium sulphate for ammonium sulphate produced intense blues comparable to those made from mixed potassium and sodium salts. In all substitutions bronze was apparent.

Vigorous oxidation of the intermediate paste produced bronzy pigments and reduced particle size. The vigorous oxidation was obtained by:

1. use of strong oxidizing agents,
2. use of excess of oxidizing agent,
3. rapid addition of the oxidant.

The formation of the paste from dilute solutions of sodium ferrocyanide and ferrous sulphate produced finely divided bronzy pigments.

The addition of the ferrocyanide to the ferrous sulphate and ammonium sulphate resulted in a final pigment which is granular in structure with decreased bronze and tinting strength.

The formation of the paste and its subsequent oxidation at low pH values produced fine grained, bronzy blues. The optimum value for non-bronze blue was found at a pH of 5.50.

The presence of sodium cyanide and sodium ferricyanide in the sodium ferrocyanide resulted in bronzed blues which were partially peptized.

X-ray investigation failed to show any difference between samples of bronze and non-bronze blues.

Blue pigments made from the α or β configurations of sodium ferrocyanide singly showed no appreciable difference in bronze.

Drying conditions of the pigment influenced the tinting strength, hardness, oil absorption, and bronze. An optimum drying condition was found at 65°C and a relative humidity of 50 percent.

Thermoageing of the pigment or other factors tending to produce peptization resulted in bronzy blues.

A low refractive index of the vehicle promoted bronzing tendencies of a pigment.

The addition of black pigments to the blue tends to decrease the intensity of reflected light and tends to decrease visible bronze.

Bronze was found to be a volume characteristic of the film as well as a surface phenomenon by investigation of lacquer films.

CONCLUSIONS

An analysis of the entire investigation indicates that the bronzing characteristics of a prussian blue pigment are primarily dependent on particle size and the vehicle employed. The optimum conditions for the making of a non-bronze prussian blue pigment involves the production of a particle not smaller than 1 μ in diameter but fine enough to hold the tinting strength.

For the formulation of the pigments investigated in this thesis, optimum conditions for the elimination of bronze were:

1. concentrated solutions of ferrocyanide and ferrous sulphate, the former being added to the latter,
2. an oxidation temperature of 25°-30°C,
3. ammonium sulphate contents between 0.5 and 1.5 mols per mol of sodium ferrocyanide,
4. a pH of 5.5,
5. drying at 65°C, relative humidity of 50 percent.

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