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Coalesced Phthalocyanine Pigments for Paints

Progress Report

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TABLE OF CONTENTS

Coalesced Phthalocyanine Pigments for Paints
(Project Number 1311)

A. J. Johnson

JLR-59-1, No. 48 Serial Number 18822
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Objects of the Investigation

1. To investigate the preparation of shaded extended phthalocyanines by co-baking phthalonitrile and copper salts with tinted extenders.

2. To improve Pigment BX-CR and study the mechanism of the reaction by which it is formed.

3. To determine the nature of the new pigment (Green Z) obtained by baking phthalonitrile, cupric chloride and zinc oxide.

4. To prepare representative samples of various extended phthalocyanines, using the co-baking technique, for evaluation by the Pigments Department.

Period Covered by the Report

Nov. 24, 1942 to Jan. 15, 1944.

Historical Background:

In a joint investigation which is being carried out by Jackson Laboratory and the Pigments Department, it was found that various phthalocyanines prepared by co-baking, in the presence of various extenders possessed properties which made them appear to be of considerable interest as inexpensive, non-flocculating phthalocyanine pigments for the paint industry. One of the most interesting of these products is Pigment BX-CR, which is the coalesced pigment obtained by co-baking phthalonitrile, cupric chloride and TiO_2 in the proportions to give a combination of one part Monochloro CPC with three parts of TiO_2. This product is greener, duller and weaker than a 1:3 mechanical mixture of "Monastral" Fast Blue BX and TiO_2. It was one object of the work described in this report to

improve the shade, brightness and yield as well as to correct other undesirable properties of the product, namely, reactivity with certain paint vehicles ("gelling") and corrosion of metal surfaces during ball-milling of lacquer grinds made with Pigment BX-CR.

Another product which seems to be of considerable interest is the dull, olive-green pigment obtained by replacing the titanium dioxide in a BX-CR co-bake by zinc oxide. It was one object of this work to make a study of the composition of this pigment and the mechanism of its formation.

Since there is a definite need for a reddish blue pigment of the Phthalocyanine class it was another object of this work to investigate the possibilities of preparing coalesced reddish-blue pigments by incorporating various red shading colors in BX-CR co-bakes.

This work was carried out in co-operation with the Pigments Department in Newark where the products prepared in Jackson Laboratory are being evaluated by extensive flocculation and exposure tests in various paint formulations. A number of the samples prepared in this work were made on various brands of titanium dioxide and other extenders furnished by the Pigments Department for this purpose. A few of the baking experiments included in this report were carried out in earlier work on coalesced phthalocyanine pigments by G. B. Robbins. Most of the earlier work on the development of coalesced phthalocyanine pigments was reported in the following Jackson Laboratory reports:

JLR-59-1, No. 46, Serial Number 18406, G. B. Robbins
Extended Phthalocyanine Pigments
(Pigment BX-CR)

JLR-59-1, No. 47, Serial Number 18772, N. M. Bigelow
Preparation of Extended Phthalocyanine Pigments
by Protracted Milling.

Conclusions:

1. Most red shading components tested to date, were destroyed in the co-baking step. Ponsol Brilliant Violet 4RN and Violet DX (the dioxazine from chloranil and beta-naphthylamine) are the most satisfactory but even with these there is objectionable dullness and weakness in the co-baked products.

2. No conditions for improving the brightness and strength of Pigment BX-CR have been found. Our analytical tests have indicated that the reaction is far from complete, being from 60-75% of theory, and that "gelling" in certain formulations is due to organic impurities and that corrosion is due to mineral acid or excess cupric chloride remaining in the crude bakes.

3. The product obtained by co-baking phthalonitrile, cupric chloride and zinc oxide (Green Z) consists of CPC (not Monochloro CPC) which is formed in a yield of about 50% of theory, and a dark yellowish green component which is readily destroyed by mineral acid. Green Z possesses excellent light fastness and is of definite interest as a pigment for paints.

4. A large number of samples have been prepared at the request of the Pigments Department for detailed evaluation. Some of these preparations were confirmatory experiments, duplicating previously submitted samples, while others were made with newly proposed extenders, some of which were supplied by the Pigments Department. Nothing of outstanding interest was obtained in this work.

Summary

A. Red Shade Phthalocyanines

A number of tinted extenders were tested as possible sub-strata to obtain reddish-blue shades of CPC by the co-baking method. Most organic coloring matters were destroyed during the baking due to the high temperature and the effect of acid fumes evolved during the reaction. Ponsol Brilliant Violet 4RN, which is used as a shading component in the production of "Monastral" Fast Blue 2R, and Violet DX, a dioxazine color obtained from chloranil and beta-naphthylamine, were found to withstand the baking treatment fairly well, but the resulting pigments are somewhat duller than mechanical mixtures of the pigments and the corresponding TiO_2 extenders. The best method for extending Ponsol Brilliant Violet 4 RN on TiO_2 is by vatting the color in a slurry of the white pigment and then oxidizing by blowing with air. In the case of the Violet DX this method was not applicable and the co-acid-pasting of the color and the TiO_2 was found to give good results. Sulfanthrene Red 3B was found to be fairly stable under baking conditions but it did not have enough tinctorial power or the correct shade to be of value as a tinting agent for red-shade CPC.

B. Co-Bakes of Monochloro-CPC and Yellow Extenders.

A number of co-bakes were made using various yellow pigments furnished by Krebs and in most cases also some TiO_2. The resulting greenish pigments have been evaluated by the Pigments Department. After 15 weeks of exposure in New Jersey all of the yellow components have faded, contrary to their behavior under the Hanovia lamp. The co-baked products and the mechanically mixed controls show fading to the same degree. No advantage is achieved by the co-baking process.

C. Pigment BX-CR

From the earlier tests on extended pigments prepared by the co-baking method, the product obtained by co-baking a mixture of phthalonitrile cupric chloride and TiO_2 in the proportions to give one part of Monochloro CPC to three parts of TiO_2 was selected as the most promising combination. This product, known to us under the name Pigment BX-CR, has been the subject of further study and process development work designed to overcome some of its short-comings, such as the causing of gelling in certain paint formulations, its dullness of shade and acidity, which caused corrosion and gas-formation when milled with paint vehicles in steel ball mills.

The total acidity of our first Semi-Works charge of Pigment BX-CR was found by titration with NaOH in hot aqueous suspension to be equivalent to 3.44% calculated as hydrochloric acid, which is more than can be accounted for by the total chlorine in the cupric chloride. It is quite evident that a large part of the acidity is due to degradation products of phthalonitrile since only a slight mineral acid acidity was indicated by test papers. One of the degradation products in Pigment BX-CR has been identified as phthalimide. Its presence in any appreciable amount causes a "bloom" to appear on the surface of paint films. Extraction of Pigment BX-CR with various solvents, such as acetone, water, pyridine or dilute caustic soda, corrects the corrosion of metallic surfaces and also gelling in all cases except acetone. Since the latter solvent did not remove the inorganic salts it is indicated that these are the cause of gelling.

Various modifications were made in Pigment BX-CR co-bakes in an effort to produce an improved product. A number of runs were made with copper bronze, cupric and cuprous oxides and cupric hydroxide. All of these products

were green, dull and weak when compared with a mechanical mix of Monastral Blue BX and TiO_2. In view of the fact that all of these products were chlorine-free it was expected that the shades would be redder than the above standard. The tinctorial weakness of the samples indicates that the yields of CPC must have been below normal. A series of runs in which methyl-glucamine was added to co-bakes with copper bronze, cupric and cuprous oxides gave products that were much duller than similar runs without this assistant. The presence of other bases such as calcium carbonate, ammonia and triethanolamine, in BX-CR co-bakes caused weakness and dullness. The use of cupric chloride in the form of the salt $CuCl_2$:2 pyridine gave a non-gelling and non-corroding product, that was slightly greener and duller and slightly weaker than Pigment BX-CR. By heating Pigment BX-CR in vacuum at 180-210°C for 2 hours or by baking for 10 hours, instead of 2 hours, the pigment lost its corrosive property, but not its gelling property, and the product became weaker and duller. The use of purified phthalonitrile or ammonium molybdate as a catalyst did not give improved products. The exposure of Pigment BX-CR to ammonia fumes at room temperature overcame the corrosion property but did not correct the gelling.

Analysis of Pigment BX-CR

An analysis of this product for total and extractible copper and nitrogen showed that 10.5% of the total copper and 18.2% of the total nitrogen were extractible by dilute ammonia and water, respectively. Other samples prepared for analysis by acid-pasting Pigment BX-CR and extracting with dilute caustic soda and ammonium hydroxide and by extracting the color from the TiO_2 by means of concentrated sulfuric acid gave copper and chlorine analyses that were fairly close to the theoretical values for Monochloro-CPC but the nitrogen was somewhat higher. The analysis of the co-baked product for Monochloro CPC was carried out by extraction of the pigment by means of concentrated sulfuric acid, using a fine-grained sintered glass crucible for the filtration. The color obtained by drowning in water was filtered on a Gooch crucible with an asbestos mat, washed with water, alcohol and acetone to remove soluble organic matter. By this method the yield of Monochloro CPC in Pigment BX-CR (S.W. Charge No. 1) was found to be 75.1% of theory. A similar analysis of a 1:2 co-bake of Monochloro CPC and TiO_2 indicated a yield of 79.3% of theory, whereas that of a 1:20 co-bake was only 40.75% of theory. These results showed that the higher the dilution

with TiO_2 the lower is the yield of Monochloro CPC.

Other Means of Baking Extended Pigments

A number of co-bakes were carried out in a 1-liter iron pot heated in an oil-bath. It was found that bakes could be carried out in this type of equipment provided the agitator had a narrow clearance from the sides and bottom of the pot. It was found that the charge was somewhat sticky when the reaction and color formation started, but after a short period the charge was again friable and easily stirred. During the subsequent stirring and heating unchanged phthalonitrile sublimed out of the charge and collected on the lid.

An experimental continuous baker was made by mounting a 1-inch(diameter) glass combustion tube in an electric furnace. A continuous feed was provided by a heavy wire spiral having 15 turns in 12 inches and which was rotated at a speed of 2 revolutions per minute and provided with a hopper for charging in the pre-mix. With the furnace set at 200°C a 1:3 pre-mix was fed in. After 5 minutes the baked product was being discharged. After running for 1/2 hour longer the spiral could no longer be turned. The sticking was mainly due to the solidification of phthalonitrile on the cooler part of the tube near the exit of the furnace. The results obtained with this apparatus, while not entirely satisfactory, indicated that the process was feasible. In order to be operative it would have to be provided with a propelling device of sufficient mechanical strength and a scraping action to keep the sides of the tube clean and free from sublimed material in the cooler portions of the exit tube. Another way would be to keep the tube hot enough on the exit and to prevent condensation of sublimed material. To design a workable unit would require a study of the thermodynamics as well as mechanical problems since the temperature control would involve balancing the heat input required to start the reaction and the heat evolved during the reaction. It is possible that enough reaction heat is evolved that a properly designed unit would not require any outside heat to carry on the process once it has been started.

D. Green Z

This coalesced pigment, known to us under the name "Green Z", is obtained by co-baking phthalonitrile, cupric chloride and zinc oxide in the proportions to give a Monochloro-CPC:Zno ratio of 1:3. The product is a dark olive-green colored pigment which the Pigments Department considers to be of special interest on account of its unique shade and good fastness properties.

It was found that on treatment with acid the color quickly changes to a blue and on dissolving the zinc oxide in acid the blue pigment that remained was found to be CPC and not Monochloro-CPC as had been expected, since cupric chloride had been used in its preparation. By this extraction method it was found that the yield of CPC was only about 50% of theory. Increasing the amount of cupric chloride by 100% gave a decreased yield, 40% of theory. The use of cuprous chloride increased the yield to 63% of theory, but the shade was bluer and brighter, which in this case was undesirable. These results indicate that the low yield is apparently due to the chlorine which is released from the copper chloride during the CPC formation, and which reacts with the zinc oxide liberating oxygen. It was found that about 90% of the total chlorine was present in a water-soluble form ($ZnCl_2$) in the co-baked pigment. A dry chlorination of Green Z showed that the color is destroyed by this treatment.

The diluting effect of the zinc oxide on the reaction is indicated by the following table:

Estimated Ratios CPC:ZnO	Yield CPC %
1:1.5	55.0
1:3	46.4
1:6	25.2
1:20	7.15
1:100	trace

Various grades and types of zinc oxide were used in the preparation of samples of Green Z to determine the effect of quality and particle size. Tests reported to date by the Pigments Department show no appreciable difference between the samples.

It was found that a nickel baker gave a color superior to that obtainable from a Monel or iron baker. A final sample (J-59-F-77-A) was made in a nickel baker and run through a micropulverizer as the only finishing step.

In an attempt to determine the nature of the reaction in the formation of Green Z, various bakes were made. A bake of a pre-mix of PN and ZnO in 4:1 molar ratio and with 1 part of salt based on PN gave a 7.8% yield of zinc phthalocyanine. The crude product, water-extracted, was a green, which turned blue when acidified. Another pre-mix as above, except that 6% (based on PN) of methyl glucamine was added, gave a 68% of zinc phthalocyanine. The crude baked product in this case was a blue. The acid-extracted color analyzed 98.5% pure by zinc analysis and 96.0% pure by nitrogen, which is considerably purer than any previously prepared product.

A co-bake of a pre-mix of PN, zinc oxide and methyl glucamine, calculated to give a coalesced ZnPC:ZnO pigment corresponding to Green Z but containing zinc phthalocyanine in place of CPC, was found to be very light and very blue in masstone as compared with Green Z. Compared with Pigment G-CR (coalesced Metal Free Phthalocyanine), the product is very blue and dark in masstone, very blue and bright in shade and weaker in strength. These results give further evidence that the color of Green Z is not due to the formation of zinc phthalocyanine and that it is due to the synthesis of a new coalesced pigment or by-product formed by a reaction which appears to involve the chlorine of the cupric chloride.

A Monochloro CPC pre-mix containing a molar equivalent of zinc oxide based on the cupric chloride used, gave a 62% yield of CPC containing only 0.68% of chlorine (theory for Monochloro CPC is 5.82%). These results showed that zinc oxide even in comparatively low concentration decreases the yield of CPC and prevents the formation of Monochloro CPC.

A pre-mix as above, except substituting copper sulfate (anhydrous) for the cupric chloride, gave a 54.4% of theory yield of CPC, which was greener in appearance than the above product, where cupric chloride was used.

In an attempt to find the source of the yellowing component in Green Z by studying the effect of heat at the baking temperature on the various ingredients of the pre-mix, several bakes were carried out without phthalonitrile being present. Zinc oxide baked alone showed no change in color,

nor did a mixture of zinc oxide and cupric chloride or a mixture of cupric chloride, zinc chloride and zinc oxide. When a mixture of benzonitrile (a possible impurity in phthalonitrile), cupric chloride and zinc oxide was heated in a test tube in an oil-bath at 200-210°C. for 2 hours, most of the benzonitrile had distilled out, leaving the residual reaction mass slightly darkened to a light brown.

E. Co-bakes of CPC on Various Extenders

In the earlier part of this work a number of co-bakes were carried out using cuprous chloride, PN and various white extenders. Since these products were all greener than mechanical mixtures of CPC and the white extenders, later work was confined to pre-mixes using cupric chloride, which is more readily obtained and handled than the cuprous chloride.

Co-bakes of Monochloro CPC in Various Extenders.

A number of co-bakes of Monochloro CPC were carried out, using various extenders, many of which were supplied by the Pigments Department. Pigments prepared by co-baking Monochloro CPC on Blanc Fixe, Barytes, asbestine, talc and silica were found to show no advantage over mechanical mixtures of the same components. Monochloro CPC cobaked on lithopone is intermediate in its properties between a mechanical mixture and a true coalesced pigment. Antimony trioxide gave a truly coalesced pigment, which resembled Pigment BX-CR in most of its properties. The pigment obtained by co-baking Metal Free Phthalocyanine and Ultramarine Blue in a ratio of 1:19 was found to be of considerable interest and other samples in different ratios will be prepared for further tests.

Patent Situation

A survey on coalesced pigments by the co-baking technique is being made by another chemist and will be reported by E. E. Beard. Patent memoranda will not be written until more data have been obtained.

Plans for Future Work:

Further work on the improvement of Pigment BX-CR is being continued under a specific project, (J-59-8). Further exploratory work on coalesced phthalocyanine pigments is in progress and will be reported under Project J-59-1.

Experimental

(A) Red-Shade Phthalocyanines

The reddest shade of the phthalocyanine blues is Monastral Fast Blue 2R, which consists of CPC containing 17% of Ponsol Brilliant Violet 4 RN. To obtain the maximum value of the vat shading color it is co-acid-pasted with CPC. It was the object of this work to determine the possibility of preparing red-shade extended CPC pigments by the co-baking method, carrying out the CPC formation in the presence of various tinted extenders. The results of the most important of the runs made are tabulated in Table I.

Table I

Shaded Extended CPC Pigments

JLNB No.	Ratio Cl CPC TiO_2	Shading Color on TiO_2 Color	%	Shade	Remarks
4018 44	1:3	Ni dimethylglyoxime	18	Nearly black	
45	1:3	" " "	18	Nearly black	
46	1:3	Cadmium Red	25	V. green, V.dull	
52	1:3	Ponsol Brilliant Violet 4RN	15	Sli.green, sli.dull	Color vatted & oxidized in slurry of TiO_2.
53	1:3	Helio Fast Pink RLA	4.7	Green, v.dull	
54	1:3	" " " "	4.7	Red, dull	
55	1:3	Ponsol Brilliant Violet 4 RN	15	Green, dull	As in 52
56	1:3	Cadmium Maroon	25	Green, dull	
59	1:3	Ponsol Brilliant Violet 4 RN	15	Greener, duller	Color and TiO_2 co-acid-pasted.
70	1:3	Ponsol Brilliant Violet 4 RN	15	Lighter, greener, duller	As in 52
72	1:3	Violet DX	16.7	Redder, duller, darker	As in 59
75	1:3	Violet DX	16.7	Greener, duller sl. darker	Color & TiO_2 ball-milled wet.
76	1:3	Lithosol Bordeaux Bl Paste	15	Green	Color & TiO_2 co-slurried
80	1:3	Ponsol Brilliant Violet 4 RN	25	Redder, duller	As in 52 MDD-491
81	1:3	Isodibenzanthrone	20	V.dull, lighter	As in 59
92	1:3	Ponsol Brilliant Violet 4 RN	17	Sli.green, redder	As in 52 MDD-563

Table 1 (Continued)

Shaded Extended CPC Pigments

JLNB No.	Ratio Cl CPC TiO_2	Shading Color on TiO_2 Color	%	Shade	Remarks
93	1:3	Violet DX	25	redder, duller	As in 59
97	L:3	Tetrachloro-iso-dibenzanthrone	25	dull and weak	As in 52
99	1:3	Calcium Aluminum Alizarate	10	v. green & dull	
107	1:3	Dichloro-iso-dibenza-throne	15	weak and dull	As in 59 Chlorination on TiO_2
123	1:3	Chlorinated iso-dibenzathrone	25	redder & duller	As in 59 Chlorination on TiO_2

The standard used for shade comparison was a mechanical mixture of "Monastral Fast Blue 2 R Paste (dried) and the same TiO_2 brand which was used in the corresponding co-bake. It was found that most organic colors were destroyed in the baking. The combined effect of high temperature and hydrochloric acid which is evolved in the reaction probably account for the destruction of the dyestuff. The only colors which seemed to be suitable as judged by this preliminary work, are Ponsol Brilliant Violet 4RN and Violet DX, which is the dioxazine color from chloranil and beta-naphthylamine.

Various means of obtaining good incorporation of the dyestuff with the extender were tried, such as co-ball-milling, vatting and oxidizing the color in a slurry of the TiO_2 and co-acid-pasting. In the case of Ponsol Brilliant Violet 4RN all three of these methods were tried and it was found that the vatting procedure gave the best results. In the case of Violet DX the vatting method could not be used and in this case it was found that the co-acid-pasting method gave the best results.

Even under the best conditions the co-baked products were found to be duller than mechanical mixtures of the Monastral color, the extender and the shading color. From tests reported to date by the Pigments Department it would appear that the use of shading colors either as properly dispersed toners or extended pigments would be more satisfactory than any co-baked product.

Several experiments were carried out using Sulfanthrene Red 3B as a shading color. This color, although apparently not destroyed in the co-baking step, did not have sufficient tinctorial strength to serve as a good reddening agent for Monochloro CPC. The shaded pigments were considerably dulled when Red 3B was used.

(B) Co-Bakes of Monochloro CPC and Yellow Extenders

Pre-mixers were made with varying amounts of phthalonitrile, cupric chloride and various yellow extenders. In some cases white extenders also were included as diluents. The experiments listed below were made by baking the pre-mixes at temperatures from 180 to 210° C.

Table II

Co-bakes of Monochloro CPC and Yellow Extenders

JLNB No.	MDD No.	Diluent	Ratio Cl CPC: Diluent
39 8-121-A	468	Chrome Yellow Y-469-D TiO_2	1:2:1
" 145	471	" " Y-538-D "	1:2:1
" 146	472	" " Y-299-D "	1:2:1
" 157		" " Y-469-D	1:2
" 174		" " Y-469-D	1:5
" 122	469	Zinc Yellow Y-232-D TiO_2	1:2
" 164		" " Y-232-D	1:2
" 175		" " Y-232-D	1:5
" 138	470	Ferrite Yellow TiO_2	1;2:1
" 158		" "	1:2
4169-111	685	" "	1:4

(C) Pigment BX-CR

The extended, coalesced pigment obtained by co-baking phthalonitrile, cupric chloride and TiO_2 in the proportions to give a Monochloro CPC:TiO_2 ratio of 1:3 was one of the products that was selected for possible commercial development. It was given the name Pigment BX-CR. Although this product is valuable on account of its non-flocculating property and resistance to chalking it also shows some short-comings, such as causing gelling in certain formulations, and its dullness of shade and acidity, which caused corrosion and gas-formation when milled in contact with metal.

A titration of a 25 g. sample of BX-CR (Semi-Works Chg. #1) with caustic soda required 23.5 cc. of N/1 caustic solution, which when calculated as hydrochloric acid amounted to 3.44% of HCl. If all of the chlorine of the cupric chloride would be converted to hydrochloric acid it would amount to 3.00%. Since it is known that some hydrochloric acid is evolved during the baking and that a part of the chlorine appears in the CPC formed, it is evident that only a part of the acidity can be accounted for by that of the cupric chloride used. A part of the acidity was undoubtedly due to the presence of degradation products of phthalonitrile. One of the degradation products has been identified as phthalimide.

The results of extraction of Pigment BX-CR with various solvents are tabulated below:

Table III

Extraction of Pigment BX-CR with Various Solvents

JLNB 4169	Solvent	Method	Insoluble %	vs. mechanical mix			
				Shade	Strength	Gelling	Corrosion
44	Acetone	Soxhlet	93.6	Green & dull	Cons. weaker	Considerable	None
47	Pyridine Bases	Soxhlet	92.2	Sli.green & dull.	Sli. weaker	None	None
50	Water	Slurry 85°C.	90.7	Duller	Sli. strong	None	None
51	Dilute Caustic Soda	Slurry 85°C.	92.8	Sli. duller		None	None

The acetone extraction took out soluble organic impurities but left inorganic material and since the extracted sample gelled in the lacquer, whereas the samples extracted with water, pyridine basis and dilute caustic soda did not, it appears that the gelling is due to an inorganic impurity, probably cupric chloride. All of the solvents removed the corrosion property, which is undoubtedly due to acidity.

A number of bakes were made in an effort to improve Pigment BX-CR either in shade and brightness or freedom from gelling and corrosion. The results are given in Table IV.

Table IV

Modified Pigment BX-CR Co-bakes

JLNB NO.	Variation	Comparison with mechanical mix Blue BX + TiO_2 or Pigment BX-CR (marked *)				
		Shade	Strength	Gelling	Settling or Sediment	Corrosion
4018-184	Cu bronze	greener, duller			trace	
4069-22	Cu bronze 100% excess	v. green, v. dull			slight	
" -25	As above + methyl glucamine	green, v. dull			slight	
" -27	Methyl glucamine	green, dull			slight	
" -31	Cupric Oxide	too weak to judge	v. weak		v. cons.	
" -33	As above + methyl glucamine	green, dull	weak		v. cons.	
" -35	Cuprous oxide	green, dull			cons.	
" -37	As above + methyl glucamine	green, v. dull			trace	
" -43	$CaCO_3$ added	*too weak to judge	v. weak	v. severe	none	none
" -46	Triethanolamine added	m. greener, duller	m. weaker			
" -52	Cupric hydroxide	sli.green, v. dull	sli. weaker		negligible	none
"-108	NH_3 after baking	m.greener, v.m. duller	m. weaker	none		none

Table IV (Continued)

Modified Pigment BX-CR Co-bakes

JLNB No.	Variation	Comparison with mechanical mix Blue BX + TiO_2 or Pigment BX-CR (marked *)				
		Shade	Strength	Gelling	Settling or Sediment	Corrosion
4069-109	NH_3 during baking	v.m. greener, v.m. duller	v.m. weaker	none		none
" -116	Purified PN	*similar	similar		equal	
" -120	Ammonium molybdate as catalyst	*similar	similar		equal	
" -121	$CuCl_2$.2 Pyridine	*sli.green & dull	sli. weak	none	equal	none
" -129	Heated in vacuum	m. greener & duller	v. weak	serious		none
" -132	Baked 10 hours	*dull	v. weak	severe	slight	none
" -133	Exposed to NH_3	m. greener & duller	v. weak	serious		none

The corrosion property was overcome by elimination of acidity either by using copper in other forms than the chloride or by using a base during or after the co-baking. Extended baking or heating in a vacuum also prevented corrosion. In all of these treatments, however, dullness and weakness developed.

The gelling property was not as readily corrected. Only when the product was heated in the presence of a base such as ammonia or pyridine was the gelling property eliminated. Heating in vacuum, which removed an organic impurity, or heating in the presence of a weak base such as $CaCO_3$ was not effective in over-coming gelling. These results indicate that the gelling is due to inorganic salts, as was concluded earlier from extraction results (see discussion following Table III). We failed to obtain any indication in the variations tried (listed in Table IV), that a redder and brighter coalesced pigment could be obtained. Methyl glucamine has a distinctly greening and dulling effect. The phthalonitrile (PN) used in 4169-116 was purified by crystallization from acetone, after filtering from insoluble impurities.

Analysis of Pigment BX-CR

In order to determine the course and extent of the reaction in the co-baking procedure it was thought advisable to analyze the product. An analysis of the crude product for total and extractible copper and nitrogen using dilute ammonia for the copper extraction and water for the nitrogen extraction gave results indicating that an appreciable amount, 10.5% of the total copper and 18.2% of the total nitrogen, was extractible. But with these corrections the copper analysis indicated a purity of 104.3% and the nitrogen analysis a purity of 84.3%, as shown below:

Table V

Analysis of Pigment BX-CR

			Copper			Nitrogen					
	Total	Ex-tract-ible	Net	Theory for ClCPC	% Theory	Total	Ex-tract-ible	Net	Theory for ClCPC	% Theory	Fo
Pigment BZ-CR Chg #1	3.04	0.32	2.72	2.605	104.3	4.73	0.86	3.87	4.59	84.3	
4169-107 Acid-pasted & alkali-extracted	1.82			2.605	69.9	4.29			4.59	93.5	1.
4169-122 ClCPC extracted by H_2SO_4	8.88			10.41	85.3	18.42			18.35	100.3	4.

An acid-pasted sample (4169-107) in which the product was subjected to two alkali slurries, one with dilute caustic soda and one with dilute ammonium hydroxide solution, the analysis for copper and chlorine were fairly close, indicating 69.9 and 72.9% of theory, respectively, but the nitrogen analysis was noticeably higher, being 93.5% of theory for Monochloro CPC.

In experiment 4169-122, the Monochloro CPC was separated from the TiO_2 by extraction with concentrated sulfuric acid and filtering the sulfuric acid solution on a sintered glass funnel, followed by recovering the pigment by drowning the filtrate in water, filtering off, washing and drying. The nitrogen analysis again was higher than that for copper and chlorine. Additional analyses for total pigment were carried out by extracting small samples with concentrated sulfuric acid, using fine-grained sintered glass crucibles for the acid filtration and Gooch crucibles with asbestos mats for filtering off the drowned color, washing with water to remove acid and with alcohol and acetone to remove organic soluble matter. By this method the yield of Monochloro CPC in Pigment BX-CR (Semi-Works Chg. No. 1) was found to be 75.1% of theory.

A similar analysis of a 1:2 co-bake of Monochloro CPC and another brand of TiO_2 indicated a yield of 79.3% (4169-140) of theory whereas that of a 1:20 co-bake (4169-135) was only 40.75% of theory. These results showed that the higher the dilution with TiO_2 the lower is the actual yield of Monochloro CPC.

Other Means of Baking Pre-Mixes.

A number of co-bakes were made in equipment other than rotary bakers. (e.g. JLNB 4018-47, 48, 51, 73 & 77). Some of these were carried out in a metal pot heated in an oil-bath and having an agitator that had a narrow clearance from the sides and bottom. It was found that the charge was somewhat sticky when the reaction and color formation started and after a short period the charge was again friable and easily stirred. During the subsequent stirring and heating unchanged phthalonitrile sublimed out of the charge and collected on the lid. In order for this type of equipment to be successful it is necessary to have an agitator that has as small a clearance from the bottom and sides as possible, since the portion of the charge that is next to the hot sides and bottom, if not moved, loses its phthalonitrile before the reaction temperature is reached and the ClCPC is not formed.

A continuous type of baker was made by mounting a glass combustion tube (1 inch diameter) in an electric combustion furnace. A continuous feed was provided by a heavy wire spiral having 15 turns in 12 inches and which was rotated at a speed of 2 revolutions per minute and provided with a hopper for charging in the pre-mix. With the furnace set at 200°C a 1:3 pre-mix was fed in. After 5 minutes the baked product was being discharged. After running for 1/2 hour longer the charge became too stiff and the spiral could not be turned. The sticking was mainly due to the solidification of phthalonitrile on the cooler part of the tube near the exit of the furnace. The product was much superior to a mechanical mix in resistance to chalking, as judged by exposure tests under a Hanovia lamp. The masstone of the crude product was greener and lighter than a mechanical mix and greener and darker after milling in a ball-mill. Undoubtedly a continuous baker could be built which would operate satisfactorily. In order to be operative it would have to be provided with a propelling device of sufficient mechanical strength and a scraping action to keep the sides of the tube clean and free from sublimed material on the cooler portions of the exit tube.

(D) Green Z

The coalesced pigment obtained by co-baking phthalonitrile, cupric chloride and zinc oxide in the proportions to give a Monochloro CPC:ZnO ratio of 1:3 is a dark olive-green pigment which the Pigment Department considers to be of potential commercial value. It has been named Green Z.

In preparing a large sample (4018-127) similar to an earlier sample (MDD-466) an iron baker was used. Since the product was bluer and duller than the original sample, a series of runs was made using Monel, nickel and iron bakers. The experiments baked in the Nickel baker (4018-156-C) showed the brightest and best tint and a large sample was prepared from a composite of runs made in the Nickel baker. This sample, 4018-158, was submitted as Final Sample J-59-F-77-A.

The results of these and other co-bakes are given in Table VI.

Table VI

Green Z CPC:ZnO 1:3

JLNB No.	Ratio CPC: ZnO	MDD No.	Masstone	Shade	Strength	Remarks
4018-						
127	1:3		Dark green	Dull		Similar to MDD 466 J-59-F-77 Iron Baker
153	1:3	612	Greener			100% excess $CuCl_2$
156-A	1:3		Dark green	Sli.bright	Equal	Monel baker
156-B	1:3		Dark green Sli. dull	Duller	Equal	Iron baker
156-C	1:3		Dark green	Sli.bright	Equal	Nickel baker
158	1:3					J-59-F-77-A Nickel baker
166	1:3	619	Greener			Pigment type ZnO ZZZ-55
173-A	1:3	614				Cu_2Cl_2 used Yield CPC 63%
173-B	1:3	615				Cu_2Cl_2 used Extracted with water.
174	1:3	613				Extracted with water
178	1:3			Sli.bluer, sli.brighter		Cu_2Cl_2 used

Table VI (Continued)

Green Z CPC:ZnO 1:3

JLNB No.	Ratio CPC: ZnO	MDD No.	Masstone	Shade	Strength	Remarks
4018-179	1:1:2*		Much greener & duller than mix			*1:1:2 CPC:ZnO:R.610
182	1:2:1*		" " " " " "			*1:2:1 CPC:ZnO:R.610
4169-8	1:3		Green, sli. light	Green, dull	v.weak	Methy glucamine added
10	1:3	620				ZnO - Av. Size 0.35-0.45 micron Horsehead XX-3
12	1:3	621				ZnO - Av. Size 0.6-1.0 micron Horsehead XX-503
13	1:3	622				Horsehead XX601
14	1:3	623				ZnO-Av.size 0.25-0.40 microns Florence Green Seal - 8
15	1:3	624				ZnO-Av.size 0.11-0.17 microns Kadox Black Label -15
17	1:3	625				ZnO-Av.size 0.4-0.6 microns 35% Leaded ZnO
38	1:6	643				25.2% yield CPC
40	1:20	644				7.15% yield CPC

Table VI (Continued)

Green Z CPC:ZnO 1:3

JLNB No.	Ratio CPC: ZnO	MDD No.	Masstone	Shade	Strength	Remarks
4169-41	1:3	645				Cuprous oxide added
49	1:1 1/2	642				55% yield CPC
167	1:100	746				Extender very slightly tinted.

An analysis of J-59-F-77-A by extracting out the diluent and by-products with dilute hydrochloric acid and acetone indicated a yield of pigment of 46.4% of theory. Similar analyses of a number of samples averaged about 50% of pigment, and the pigment was mainly chlorine-free CPC and not Monochloro CPC as has been assumed would be formed since cupric chloride had been used.

In experiment 4018-153 where a 100% excess of cupric chloride was used, the yield was only 40% of theory. When cuprous chloride was used (Experiment 4018-173-A), the yield was 73% of theory. The results of these runs showed that the low yield was due to the effect of the chlorine. An analysis of J-59-F-77-A showed that 87.8% of the chlorine originally in the pre-mix was in a water-extractible form indicating that it had reacted with the zinc oxide during the baking. Since this reaction had taken place, oxygen must have been liberated and it is probable that at the high temperature of the reaction this had a destructive effect on the organic compounds present.

That the zinc oxide had also a "diluting" effect on the reaction is evident by comparing the yields where various amounts of zinc oxide had been used, as shown in the following table:

Table VII

Green Z Co-bakes with Various Ratios of Zinc Oxide

JLNB No.	Estimated Ratio CPC:ZnO	Yield CPC %
4169-49	1:1 1/2	55.
4018-158	1:3	46.4
4169-38	1:6	25.2
4169-40	1:20	7.15
4169-167	1:100	trace

Effect of Quality of Zinc Oxide

In the earlier part of this work U.S.P. quality zinc oxide was used. In Experiment 4018-166 a pigment type was used and no appreciable difference was noted in the Green Z obtained from it. In the series from Experiments 4169-10 to 4169-17 (Table VI) various types and grades of zinc oxide were used. Some of these products were prepared from zinc metal and others were prepared directly from the ore. One brand contained 35% of lead sulfate. The average particle size varied from 0.11 micron to 1 micron. Although there was considerable variation in appearance of the various samples, no marked difference was noted in shade, strength or fastness in the earlier tests made by the Pigment Department. The results of more extended tests are not as yet available.

Zinc Phthalocyanine

In an attempt to determine the nature of the reaction in the formation of Green Z various bakes were carried out. A pre-mix (4169-2) of 130 g. PN, 20.6 g. ZnO and 130 g. salt was baked at 200-210°C. for 2 hours in a Monel metal rotary baker. 274 g. of product was extracted with hot water and gave 69.6 g. of a greenish material (A). 25 g. of this material when extracted with dilute hydrochloric acid gave only 4.1 g. of a blue product (B). The analyses of these two products were as follows:

	Zn	Cu	N
(A)	20.89	0.42	15.62
(B)	9.22	1.11	18.50

From another pre-mix (4169-5) similar to the above, except that 7.8 g. methylglucamine was added, a 67.9% over-all yield of zinc phthalocyanine was obtained. The analysis of this product was:

	Zn	Cu	N
Found	11.14%	0.075%	18.6%
Theory	11.32%	-	19.4%
Purity by Analysis	98.5%	-	96.0%

This method thus gives a zinc phthalocyanine of high purity. The pigment did not have an attractive color and was not further evaluated.

A co-bake (4169-7) was made from a pre-mix of 67 g. of PN, 235 g. of ZnO and 3.9 g. of methyl glucamine, designed to give a coalesced ZnPC:ZnO pigment corresponding to Green Z but having Zinc Phthalocyanine in place of CPC. This product was found to be very light and very blue in masstone against Green Z, blue and very bright in shade and similar in strength. Compared with the coalesced Metal Free PC (Pigment G-CR), it is very blue and dark in masstone, very blue and bright in tinting shade and weaker in strength.

Monochloro CPC Bake in the Presence of ZnO

In Experiment 4018-165 a pre-mix of 65 g. of PN, 17 g. of cupric chloride, 10.3 g. ZnO and 65 g. of salt, was baked in a Monel metal rotary baker at 200-210°C. for 2 hours. The baked product was extracted with dilute hydrochloric acid and dilute ammonium hydroxide. A yield of 45.2 g. (61.9% of theory) of CPC, containing 9.77% copper and 0.68% chlorine, was obtained. These results showed that though the amount of zinc oxide was comparatively low (one molar equivalent) its presence decreased the yield of CPC and prevented the formation of Monochloro CPC.

CPC Bake with Copper Sulfate in the Presence of ZnO

In Experiment 4018-168 a pre-mix of 65 g. of PN, 20.2 g. $CuSo_4$ (anhydrous), 10.3 g. of ZnO and 65 g. sodium sulfate (anhydrous) was baked and extracted as above. A yield of 39.7 g. (54.4% of theory) of CPC containing 9.3% copper and 0.23% chlorine, was obtained. This product was greener in appearance than Experiment 4018-165.

Effect of Baking on Green Z Ingredients

In Experiment 4018-140 a charge of 300 g. of zinc oxide was baked for 2 hours at 190-200°C. in a Nickel rotary baker. The product when discharged at room temperature was white and showed no color change due to the heat treatment. It is known that zinc oxide is yellow when strongly heated but it becomes white again on cooling.

In Experiment 4018-149 a pre-mix of 300 g. of zinc oxide and 23 g. of cupric chloride was heat-treated as above. No change in color was noted.

In Experiment 4018-164-A a pre-mix of 5.2 g. of benzonitrile, a possible impurity in phthalonitrile, 1.7 g. of cupric chloride and 22.5 g. of zinc oxide was heated in a test-tube in an oil-bath at 200-210°C. for 2 hours. Most of the benzonitrile (B.P. 190-191°C.) distilled out, leaving the residual reaction mass slightly darkened to a light brown.

In Experiment 4018-164-B a pre-mix of 1.7 g. of cupric chloride, 2 g. of anhydrous zinc chloride and 22.5 g. of zinc oxide was heated as above. There was no change in color by this treatment.

Chlorination of Green Z

An experiment (4169-57) was carried out on a dry chorination of Green Z at 150°C. After passing in chlorine at this temperature for several hours, the material formed hard lumps, with most of the color apparently destroyed. An 80-g. sample showed a 10-g. gain in weight. When slurried in water the product was not acid to Congo but acid to litmus.

E. Co-bakes of CPC on Various Extenders

A pre-mix of 450 g. extender, 135 g. phthalonitrile and 25 g. cuprous chloride was ball-milled for 16 hours and screened through a 20-mesh sieve. Portions (300 g.) were baked in rotary bakers at 180°C. for 2 hours. In each case the baked charge was divided into two portions; (A) was milled with water and slurried with ammonium hydroxide, filtered, washed, dried and screened; (B) was only screened.

The results of these co-bakes, some of which were carried out earlier, are given below in Table VIII. The comparisons were made against mechanical mixtures of CPC and the corresponding extenders.

Table VIII

Co-bakes of CPC on Various Extenders

JLNB 3998 Page No.	Extender	Flocculation	Shade	Hanovia Test vs. Mechanical Mixtures
53-A	Blanc Fixe	Poor	Masstone, sli.green & bri.	Equal
53-B	" "	"	" " "	"
54aA	Timonox	Good	Tint green, weak	Cons. superior
54-B	"	"	" " "	" "
55	Gypsum	No pigment formed		
56-A	Pptd. $CaCO_3$	Good	Masstone v.green & weak	Sli. inferior
56-B	" "	"	" " "	" "
57-A	Asbestine	Good	" v.green & dull	Similar
57-B	"	"	" " "	Superior
58-A	Lithopone	Good	Tint v.green & v. weak	Sli. superior
58-B	"	"	" " "	" "
59-A	Zinc Oxide	Good	Tint green & weak	Superior
59-B	" "	"	" " "	"
60-A	Barytes	Poor	Masstone sli.green & dull	Sli. superior
60-B	"	Fair	" " " "	" "

The Hanovia test is an accelerated aging test carried out by exposing under a Hanovia lamp, panels sprayed with paints containing the pigments in a vehicle having poor resistance to aging. This test was designed as a measure of the chalking quality of a pigment; it gave results in a comparatively very short time. The value of this highly accelerated test is very questionable. To properly evaluate a given pigment it is still necessary to make paints using various formulations and make extensive tests under exposure to various temperature and weather conditions. Such tests are being made by the Pigments Dept. on a large number of samples submitted to them under MDD numbers.

Co-bakes of Monochloro CPC on Various Extenders.

In the preparation of Monochloro CPC and various extenders in a 1:3 ratio, pre-mixes were made as follows: 450 g. of extender, 130 g. of phthalonitrile (micropulverized), and 34 g. of cupric chloride were ground in porcelain ball-mills or simply run on rollers in a bottle of suitable size with several rubber stoppers for 16 hours. For the smaller rotary bakers a charge of 300 g. of premix was used. The baked products were either screened through a 40-mesh screen, or if the charge packed in the baker, it was run through a micropulverizer, using a medium screen. No extractions were made. The results of this work are summarized below in Table IX.

Table IX

Monochloro CPC on Various Extenders

JLNB No.	Ratio ClCPC: Extender	Extender	MDD No.	Shade	Strength	Gelling	Setling	Flocculation	Remarks
3998-88	1:3	Timonox	460	Green tint	weak			Good	Hanovia test-superior
99-C	1:3	Blanc Fixe	461	Jet	sli. stronger			Good	Superior(bronzed)
123	1:1	Blanc Fixe	462						
131	1:3	Pptd.$CaCO_3$	463	Milky,dull	weak			Good	Superior sli.chalk No bronze
132	1:3	Asbestine	464	v.milky, v.dull	v.weak			Good	Much superior
134	1:3	Lithopone	465	green	v.weak			Good	notic. superior
135	1:3	Zinc Oxide	466	dark green, dull	weak			Good	cons. superior
4018-49	1:1:2	Iron Oxide		nearly black			Some		
95	1:1	TiO_2	561						
101	1:1	Blanc Fixe	562						
106	1:2	Filtercel	595			None	None		
125	1:3	TiO_2							J-59-F-76 Similar to MDD 445
148	1:3	Blanc Fixe							J-59-F-67 Part 2
175	1:3	MgO				Very bad			

Table IX (Continued)

Monochloro CPC on Various Extenders

JLNB No.	Ratio ClCPC: Extender	Extender	MDD No.	Shade	Strength	Gelling	Settling	Flocculation	Remarks
181	1:3	Asbestine	618						
183	1:3	HgO							Decomposed No PC
185	1:3	Multifex	616	Indeterminate	v.v. weak				
187	1:3	Filtercel	617						
4169-18	1:3	Ultramarine Blue	626						
21	1:3*	Ultramarine Blue	628						*MFPC
55	1:3	Santocel	660	Too weak to judge	Extremely weak	Serious	Complete	Cons.	
56	1:3	Amorphous Silica	661	Dull	V. weak	None	None	Cons.	
58	1:3	Silica GRS	662	Dull and green	V. weak	None	None	Cons.	
59	1:3	ZnS	656	Greener & duller	Weak	None	Complete	Cons.	
60	1:3	Chromic oxide(hydrated)	653	Much greener,duller	Weak	None	None	None	
61	1:3	Chromic oxide	652	Green	V.v. weak	Severe	Complete	No test	

Table IX (Continued)

Monochloro CPC on Various Extensions

JLNB No.	Ratio ClCPC: Extender	Extender	MDD No.	Shade	Strength	Gelling	Settling	Flocculation	Remarks
4169-62	1:3	Antimony Oxide	655	Greener, duller	Similar	None	None	Trace	Coalesced pigment
63	1:3	Alumina Hydrate	658	Too weak to judge	Extremely weak	None	Complete	None	
64	1:3	Zirconium Oxide	654	Too weak to judge	Extremely weak	Serious	Complete	Cons.	
65	1:3	Uncalcined TiO_2	659	Green, dull	Extremely weak	Serious	Complete	No test	
66	1:3	Lithopone	657	Green, dull	Weaker	None	Complete	Cons.	Partially coalesced Pigment
67	1:3	TiO_2	663	Trace redder	Slightly stronger	Some	Complete	Cons.	
72	1:2	TiO_2							Similar to J-59-F-68
75	1:20	TiO_2							
93	1:19*	Ultramarine Blue	690						*CPC
97	1:19*	Ultramarine Blue	691						*MFPC

Table IX (Continued)

Monochloro CPC on Various Extenders

JLNB No.	Ratio ClCPC: Extender	Extender	MDD NN.	Shade	Strength	Gelling	Settling	Flocculation	Remarks
4169-137	1:3	Blanc Fixe	709						
148	1:3	Blanc Fixe	744	Similar	Weaker	None	None		Similar to J-59-F-67

Literature and References

1. JLR-J-59-1, No. 46; Serial No. 18406

   JLR-J-59-1, No. 47; Serial No. 18772

2. JLNB Nos. 3998, 4018 & 4169

3. Two Conference Reports on joint conferences of Orchem and the Pigments Department, written by N. M. Bigelow, dated September 27, 1943 and January 28, 1944, respectively.

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