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Dr. H. W. Filey (2)
Dr. E. K. Bolton (1)
Dr. William Kirk (1)
Mr. A. J. Wuertz
for I.G.I. (3)
for C.I.L. (1)
J. L. Files (2)
Dr. O. Stallmann (1)

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E. I. DuPont de Nemours & Company

Jackson Laboratory

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The Preparation of Extended Phthalocyanine Pigments by Protracted Milling

Progress Report

N. M. Bigelow
A. J. Johnson

N. M. Bigelow

O. Stallmann
Division Head

The Preparation of Extended Phthalocyanine Pigments by Protracted Milling (Project Number 1311)

N. M. Bigelow

JLR-59-1, No. 47 Serial Number 18772

Object of the Investigation:

To prepare extended phthalocyanine pigments having increased resistance to chalking or the property of chalking without marked change in shade, by the protracted milling of a phthalocyanine with a white, tinted or colored extender, either in the presence or absence of a third grinding agent such as salt.

Period Covered by the Report:

September 15, 1942, to June 1, 1943.

Historical Background:

In the Autumn of 1942, a collaborative program was undertaken by Orchem and the Pigments Department, whose object was to prepare extended phthalocyanine pigments having either increased resistance to chalking or the capacity to chalk without alteration of shade. Three general methods of preparing these extended phthalocyanine pigments were considered:

1. Mixing a phthalocyanine pigment and an extender by co-acid pasting. This work has not yet been reported.

2. The protracted milling of pigment and extender, either in the presence or absence of salt. This report describes the progress to date on this phase of the investigation.

3. Synthesizing the phthalocyanine pigment in the presence of the extender. The progress of this phase of the investigation is reported in JLR-59-1, No. 46; Serial Number 18406.

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Conclusions:

Extended phthalocyanine powders prepared by ball milling the crude pigments (with or without salt) together with selected paint extenders are superior in some properties to the corresponding mechanical mixtures. However, they are not truly "coalesced" products and will not be developed further at this time, pending the outcome of a complete evaluation of our "co-baked" phthalocyanine pigments which are much less expensive and highly coalesced products, particularly suited for use in paints.

Summary:

1. The preparation of extended phthalocyanine pigments by the protracted milling of crude phthalocyanines with various titanium dioxide pigments in the presence of salt yields an attractive extended pigment with certain meritorious features. The table which follows compares the properties of extended pigments prepared in this manner and the properties of pigments prepared by coalescing the color and extender by the "co-baking" technique as described in JLR-59-1, No. 46; Serial Number 18406, with those of mechanical mixtures of the same components.

TABLE I

Properties	Pigment Prepared by co-salt milling vs. Mechanical Mixture	Pigment Prepared by co-baking vs. Mechanical Mixture
Strength	Superior	Inferior
Retention of Strength on Dilution	Equal	Inferior
Gloss	Higher	Much higher
Sediment	Equal	Slightly-considerably inferior
Separation of color and extender	Superior	Much superior
Gelling	Equal	Inferior
Flocculation	Superior	Much superior
Chalk resistance	Slightly superior	Somewhat superior
Cost	Questionable, depending on the amount of salt which must be used in a plant scale ball mill	Highly favorable

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Both types of pigment have their points of superiority and inferiority, and any preference between them must be determined by the proposed use. It is quite possible that a combination of the co-baking and salt milling techniques may yield a product superior to that prepared by either method alone.

2. The protracted milling of mixtures of a crude extracted phthalocyanine pigment and an extender in the absence of salt yields a pigment which is visually stronger and brighter than a mechanical mixture of the same phthalocyanine (after acid pasting) and the same extender. The co-milled product is cheaper, since no acid pasting is involved. In the preparation of paints and lacquers, the extended phthalocyanine prepared by co-milling is similar to a mechanical mixture of acid pasted phthalocyanine and extender.

3. A wide range of shades may be prepared by the protracted milling of mixtures of a phthalocyanine, a shading agent and an extender, with or without salt.

4. Protracted milling of mixtures of a phthalocyanine and an inert extender other than titanium dioxide in the absence of salt gives a mixed pigment in which the depth of shade is much greater than that produced by the equivalent mechanical mixture of an acid pasted phthalocyanine and extender. It is believed that the co-milling somehow renders the extender more transparent, thus accounting for the abnormally deep shade.

Patent Situation:

The patent situation has not yet been studied carefully. The basic principle of co-milling with salt is disclosed in U.S. 2,212,924 (Muehlbauer, assigned to G.A.F.), and this Company is free to use the process. Patent protection is being sought for certain refinements in the process of salt milling in the absence of extenders. (See Lang and Detrick, Case 2) The process of salt milling in the presence of inert insoluble extenders probably is not patentable over this prior art unless novel and unpredictable results are obtained, which so far has not been true.

Plans for Future Work:

The preparation of new samples has been curtailed until the Pigments Department has evaluated a considerable number of samples which are described in this report. Specific samples will be prepared as a need for them is suggested by the findings of the Pigments Department.

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Experimental:

Technique

During the course of this investigation, protracted millings were carried out in one-quart, tinned paint cans, in 2- and 3-gallon iron mills, in a rubber-lined 3-gallon mill and in a 50-gallon ball mill in the Semi-Works. The preferred methods are described below.

1. Milling

The majority of the millings were carried out in one-quart tinned friction-top cans (paint cans). These cans were charged with 2000 g. of a mixture of steel balls (rejected ball bearings) and roofing nails, in roughly the following proportions: 5/16 inch balls, 360 g.; 7/16 inch balls, 720 g.; 9/16 inch balls, 720 g.; flat-headed roofing nails, 200 g. Before use, the cans were dried for several hours in an air oven at 100°C. All the ingredients used in the milling were carefully dried, since small amounts of water caused packing of the charge. The following weights were used in the milling experiments.

A. Milling with 1.5 Parts of Salt per Part of Extended Pigment

Ratio of Pigment to Extender	Gr. Pigment	Gr. Extender	Gr. Salt
1:3	25.0	75.0	150.0
1:6	14.3	85.7	150.0
1:20	4.8	95.2	150.0

B. Milling with Three Parts of Salt per Part of Extended Pigment

1:3	16.4	46.8	187.5
1:6	8.9	53.6	187.5
1:20	3.0	59.5	187.5

C. Milling Pigment and Extender Without Salt

1:3	31.2	93.8
1:6	17.8	107.1
1:20	6.0	119.0

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The materials were charged into the can, which was then rotated for the chosen period on rubber rollers rotating at such a speed that the cans made about 80-90 revolutions per minute. At the end of the milling period, the cans were opened and the charge was sifted away from the balls. Experiments which had packed were usually discarded, experience having shown that if they packed on the first milling, they would continue to repack on subsequent attempts to re-mill them. For cleaning, the cans were charged with water and scouring powder and milled for a half-hour, then washed and dried in an oven at 100° or more.

Mixtures with a pronounced tendency to pack were milled in quart cans charged with 2000 g. of cyl-pebs. Packing was very rare when cyl-pebs were used, but they battered the cans so badly that they were useless after two to four runs. Six to eight runs could ordinarily be made in a can charged with steel balls and roofing nails.

Only a few charges were made in the two-gallon iron mill. The walls of this mill were rough, and all charges packed sooner or later.

The three-gallon iron ball mill was satisfactory for most salt grinding, but was unsuitable for grinding in the absence of salt because of packing. The mill was loaded with 20 Kg. of cyl-pebs. The total weight of material to be ground was usually 2500 g. This mill ground more efficiently than the quart cans; a grinding period of 48 hours in this mill was roughly equivalent to a 88-hour period in the smaller cans.

The three-gallon rubber-lined ball mill gave very satisfactory results in salt grindings, being somewhat superior to the regular steel mill in this respect; however, protracted millings without salt tended to pack in this equipment.

The 50-gallon ball mill (G-16, 15 Building) operated satisfactorily in salt millings, but was unsuitable for milling without salt. In the experiments described in this report, the mill was loaded with 500 lbs. of cyl-pebs, one-half of its normal capacity. The total weight of charge was 50-60 pounds.

A 30-hour milling period in the 50-gallon mill was found to be equivalent to 48 hours in the 3-gallon mill, or to 88 hours in quart cans.

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2. Extraction

Extended pigments prepared by milling in the absence of salt required no extraction. These charges were merely sifted through a 40-mesh sieve, and were ready for testing. Pigments milled in the presence of salt required an extraction of some sort before they could be tested. The types of extraction which have been tested to date are listed below.

A. Extraction with Water at Room Temperature

One part of salt milled material was sifted slowly onto the surface of 8 parts of water, with vigorous agitation. The mixture was stirred vigorously until it was completely wetted out, and then for one hour more. The mixture was filtered, washed chloride-free with distilled water, dried in an air oven at 100° and brush-sifted through a 40-mesh sieve.

B. Extraction with Water and "Gardinol" WA at Room Temperature

One part of salt milled mixture was added to a solution of 0.004 parts of "Gardinol" WA in 8 parts of water, with agitation. The mixture was stirred for an hour after wetting out was complete. Then it was filtered, washed and dried as described above.

C. Extraction with Water at 95°

One part of salt milled mixture was suspended in water as already described. The mixture was heated to 90°-95° and held at this temperature for one hour. The suspension was worked up as described above.

D. Extraction with 2% Hydrochloric Acid at 95°

Two per cent hydrochloric acid was substituted for the water in method No. 3.

E. Extraction with 2% Sulfuric Acid at 70°

Two per cent sulfuric acid in method No. 3.

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Experimental Results:

Part One - Grinding Phthalocyanine Pigments with Titanium Dioxide

I. Type of Pigment

Copper phthalocyanine, monochloro copper phthalocyanine, polychloro phthalocyanine, metal free phthalocyanine, Pigment BX-CR and Pigment G-CR have been extended with titanium dioxide both with and without salt. Mixtures of certain of these pigments with other pigments not of the phthalocyanine type have also been prepared. The results of these experiments indicate that the response of all the phthalocyanine pigments is similar if not identical.

The following sets of experiments vary only in the choice of the phthalocyanine pigment. The terms "Ti-Pure" R-610, etc., refer to particular types of Titanium Dioxide Pigments, described in more detail in Section II.

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Composition of Mixture	CPC	Mono-chloro CPC	Metal Free PC	Poly-chloro CPC	Pigment BX-CR
1 PC: 3 "Ti-Pure" FF: 12 salt; extr. with hot dilute HCl	JLNB 4003-20-A MDD-424 JLNB 4077-49 MDD-452	JLNB 4077-50 MDD-453		JLNB 4139-35 MDD-599	JLNB 4077-154
1PC: 3"Ti-Pure" R-610 (no salt, no extraction	JLNB 4077-44 MDD-591	JLNB 4077-17 MDD-455	JLNB 4077-74		
1 PC: 3 "Ti-Pure" R-610: 12 salt; extracted with hot dilute HCl	JLNB 4003-20-B MDD-423 JLNB 4139-21	JLNB 4077-189		JLNB 4139-35 MDD-599	

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II. Type of Extender

The types of extender tested included "Ti-Pure" R-610, R-LL for R-610, R-110, FF, "Super-Soft FF" and LG. All of these extenders responded favorably to the milling technique. Paints and lacquers prepared from these products were all as strong or stronger (deeper) than mechanical mixtures of the same pigment and extender. Exact judgment of the strength of the extended pigment in paint or lacquer films was rather difficult, since strength and depth are easily confused. In general, it appeared that the milling process, either in the presence or absence of salt, reduced the hiding power of the extender, rendering it more transparent, and giving a fictitious strength or "depth" to the paint film. This strength vanished when the pigment was further diluted with unground titanium dioxide. As would be expected, the softer anastase pigments, FF and "Super-Soft FF", gave extended pigments with more strength of depth than the rutile extenders. The properties of paints prepared from all the various extenders were similar.

One set of samples prepared with "Ti-Pure" FF by salt milling appeared to chalk in self-shade to a far greater extent than comparable pigments prepared from "Ti-Pure" R-610. Repetition of these experiments and further similar trials, however, did not support this observation; all of the pigments chalked whiter, and to roughly the same extent as their controls. Many of these confirmatory experiments are still not reported; at the present time the factor which caused the exceptional behavior of the first experiments is still unknown.

Exposures under the Hanovia Lamp indicated that the extended pigments prepared from all the various "Ti-Pures" were noticeably superior and equally superior to comparable mechanical mixtures in chalk resistance. Actual accelerated outdoor exposure tests in non-durable vehicles do not confirm these results. It now appears that the salt milled extensions and mechanical mixtures are roughly similar in chalk resistance, and pigments extended with chalk resistant extenders are superior to those prepared from extenders with inferior chalk resistance. No tests in durable vehicles are yet available.

The experiments listed below afford direct comparisons of the response of various types of TiO_2 pigment to salt milling and to co-milling.

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Composition of Pigment	R-610	R-LL	R-110	FF	Super-Soft FF	LB
1. CPC:Ext.:NaCl 1:3:12 72 hr. extr. in 2% HCl	JLNB 4003-20-B MDD-423 JLNB 4139-21	JLNB 3865-176-A MDD-406	JLNB 4003-68	JLNB 4003-20-A MDD-424 JLNB 4077-49 MDD-452	--	JLNB 4077-42
2. ClCPC:Ext. 1:3 No salt, no extn.	JLNB 4077-17 MDD-591	JLNB 4077-46 MDD-	JLNB 4077-47	JLNB 4077-45 MDD-454	JLNB 4139-8 MDD-593	JLNB 4077-43
3. ClCPC:Ext. NaCl 1:3: 12 2% HCl 70-90°	JLNB 4077-189	--	--	JLNB 4077-50 MDD-453	JLNB 4139-9 MDD-573	--

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III. Influence of the Pigment:Extender Ratio

Three series of experiments were run in order to determine the influence of the pigment:extender ratio. In the first series, CPC and "Ti-Pure" R-610 was ground with salt for 72 hours and extracted with water at 90° (JLNB 4077-5, 8, 14). In the second series, mixtures of Monochloro CPC and "Ti-Pure" FF were ground in the same manner (JLNB 4077-15, 22, 181). In the third, Metal Free PC and "Ti-Pure" R-610 were ground without salt and tested without extraction (JLNB 4077-17, 23, 26). The results proved nothing in particular except that the depth or fictitious strength was lost partially at the higher dilutions. Grinds made at higher dilutions tended to pack more than those containing a higher percentage of phthalocyanine pigment. The pigment:extender ratio had no effect on the chalking characteristics of the mixed pigment.

IV. Influence of the Amount of Salt Used in the Grind

The use of salt in grinding phthalocyanine pigments with titanium dioxide extenders is of no great importance as far as the quality of the product as a paint pigment is concerned. The Pigments Department has reported that salt milled mixtures of phthalocyanines and TiO_2 show more resistance to flocculation than do comparable co-milled mixtures. However, this resistance to flocculation is lost when the paint is fortified with CPC or diluted with TiO_2. In most other respects, salt milled and co-milled extended pigments are very similar. Grinds made without salt are fully as strong, fully as soft and almost as bright as similar ones carried out with salt. A mixed pigment ground without salt and used without extraction naturally contains small amounts of iron and rust; but these impurities are in such small amounts that they cause no noticeable effect on the finished pigment. One other test wherein the use of salt shows an advantage is the evaluation of the mixed pigments on the ink mill. Here, pigments ground without salt are much weaker than those ground with salt, which are fully as strong, if not stronger, than equivalent mechanical mixtures of "Monastral" Fast Blue B and the proper extender. This point is of theoretical interest only, since the extended pigments are not intended for use in printing inks. It should be mentioned that in the salt grinding, the subsequent extraction plays a critical part in the development of the final strength of the product. This point will be discussed in more detail in a later part of this report.

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For direct comparisons, see JLNB 4077-4, 41, 44; and JLNB 4077-37, 39, and 40.

According to ink mill tests, the optimum amount of salt is three parts per part of total mixed pigment. Smaller amounts than this did not cause the development of full strength, while greater amounts did not increase strength further.

V. The Influence of Various Types of Extraction

The observation (see JLR-59-1, No. 46) that any drastic extraction process impaired the flexible coalescence of Pigment BX-CR suggested that the "inflexible" coalescence of salt milled mixtures of phthalocyanine pigments and TiO_2 might originally have been flexible to some extent, the flexibility having been lost during the extraction of the salt. Accordingly, a number of milder methods of extraction were tested; none of these altered the flexibility of the systems; paints prepared from the milled mixtures were non-flocculating per se, but showed flocculation when extended with more TiO_2 or when fortified with phthalocyanine.

The following experiments are comparable with respect to various methods of extraction.

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Composition of Pigment	Water at 20°	Water and "Gardinol" at 20°	Water at 75°	2% HCl at 75°	No Extraction
1 CPC: 3 R-610: 12 NaCl	JLNB 4077-3	JLNB 4077-4	JLNB 4077-5	JLNB 4003-20-B	
1 CPC: 3 FF: 12 NaCl	JLNB 4003-188	JLNB 4003-189-A	JLNB 4003-189-B MDD-572 JLNB-4007-181	JLNB 4003-20-A MDD-424 JLNB 4007-49 MDD-452	
1 Monochloro CPC: 3 R-610; no salt.	JLNB 4077-37	JLNB 4077-36	JLNB 4077-27	JLNB 4077-38	JLNB 4077-17 MDD-455

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VI. Optimum Time of Milling

Early experiments showed that the optimum time for grinding a 1:3:12 pigment:extender:salt mixture was between 60 and 72 hours in quart cans, 36-48 hours in three gallon mills and 24-30 hours in the fifty-gallon Semi-Works ball mill. In the absence of salt, a slightly longer period (about 72-80 hours in quart cans) was beneficial. At high pigment:extender ratios (such as 1:20), a milling period of about 90 hours appeared necessary for the full development of tinctorial strength.

For details, see JLNB 3865-175, 176; 4003-30, 32.

VII. Effect of the Presence of Phthalonitrile in Milling

For a period during the early stages of the investigation it appeared possible that the coalescence of extended pigments prepared by co-baking might be due to the presence of unreacted phthalonitrile in the product. To test this theory, a number of millings were made (without salt) in the presence of small amounts of phthalonitrile. These samples showed a slight but definite increase in resistance to the effects of the Hanovia lamp; but this superiority was not duplicated in outdoor exposure tests, and the idea was abandoned as worthless. For details, see JLNB 4003-156; 4077-31, 32, 33, 34, 35.

VIII. Effect of the Presence of Phthalonitrile Trimer in Milling

Following the observation mentioned in Section VII, one experiment was carried out in which CPC and TiO_2 were milled (without salt) in the presence of 1% of phthalonitrile trimer. Here again the addition to this material brought about a slight improvement in resistance to the Hanovia lamp, but the improvement was not duplicated by outdoor exposure tests, and the idea was dropped. See JLNB 4003-158.

IX. Final Sample J-59-F-79 (Monochloro CPC: "Ti-Pure" R-610, 1:3, Milled with Salt)

A ten-pound sample of a 1:3 mixture of Monochloro CPC and "Ti-Pure" R-610 was prepared by grinding a mixture of 3 lbs. of Monochloro CPC Crude E, 9 lbs. of dried "Ti-Pure" R-610 and 48 lbs. of salt for 36 hours in a 50-gallon ball mill charged with 500 lbs. of cyl pebs. The ground mixture was extracted with 6 parts of 2% hydrochloric acid at 65° for two hours. This was done in four 12-lb. batches in large-scale laboratory

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equipment. The extracted material was washed free of salt, dried at 60° in air ovens, and micro pulverized. The Technical Laboratory reported (memorandum 889-B, 8-23-43) that the flocculation and flooding behavior of this product in Dulux and lacquer systems was only slightly better than that of mechanical mixtures of the same ingredients, and that they did not consider the product of interest. The Newark Pigments Department reported that the salt ground mixture was considerably superior to an equivalent mechanical mixture in resistance to flocculation, but that fortification with Monochloro CPC or dilution with TiO_2 caused the re-appearance of flocculation. Both agencies considered the pigment of no commercial interest.

X. Salt Milling Pigment BX-CR
Final Sample J-59-F-71

The application of the salt milling technique to Pigment BX-CR produces an extended pigment which is brighter and considerably stronger than the original pigment. The milling, or possibly the extraction that follows it, removes the tendency of the original pigment to gel in paint vehicles and its tendency to form sediment. The chief loss sustained by Pigment BX-CR in the salt milling process is that it loses half of its flexibility; the salt milled coalesced pigment may be fortified with Monochloro CPC toner without the appearance of flocculation, but it can no longer be diluted with titanium dioxide.

A ten-pound sample of salt milled Pigment BX-CR was prepared in the 50-gallon Semi-Works mill. The salt milled crude was extracted with 2% hydrochloric acid in large-scale laboratory equipment. The salt-free crude was dried at 70° and micro pulverized. This sample was submitted to the Technical Laboratory as J-59-F-71. The Technical Laboratory reported that it showed no particular advantages over micro pulverized BX-CR, and recommended that it be dropped from further consideration. See Technical Laboratory Memo 890-B, 8-23-43.

XI. Salt Milled Monochloro CPC Toner
Final Sample J-59-F-81

In various phases of the work described in this report, the Technical Laboratory and the Pigments Department had need of a "soft" powder of Monochloro CPC. A 5-pound sample of a Monochloro CPC toner was prepared by salt milling Monochloro CPC Crude E in the 50-gallon Semi-Works ball mill. The crude

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salt mixture was extracted in the laboratory with 6 parts of 2% hydrochloric acid, washed until free of salt, dried in air ovens at 60-70° and micro pulverized. Ink mill tests on the product indicated that it had not had sufficient milling, since it appeared milky in masstone and weak in tint against acid pasted samples of the same crude. A sample was, however, submitted to the Technical Laboratory as Final Sample J-59-F-81. The Technical Laboratory reported (Memo 982-B, 8-23-43) that the type was of no immediate interest.

The foregoing material should not be used as an argument that a satisfactory salt milled Monochloro CPC toner cannot be obtained.

Part Two - Co-Milling Phthalocyanine Pigments With White Extenders Other Than TiO_2

Copper Phthalocyanine and Monochloro CPC were milled with a number of prime whites and white extenders other than TiO_2. These mixed pigments had no commercial advantages over mechanical mixtures of the same ingredients. One interesting effect was noted: In almost every case the co-milled product was much darker in masstone than the corresponding mechanical mixture, indicating that the co-milling process had in some manner increased the transparency of the extender. The degree of increase of transparency varied among the various extenders. Despite the academic interest of this phenomenon, it appeared to have no commercial value as applied to the phthalocyanine pigments.

The following combinations were tested:

(A) CPC Co-Milled at 1:6 Ratio with the Following Extenders:

Extender	Increase in Transparency	Reference
Aluminum Hydrate	Considerable	JLNB 4003-128
Aluminum Oxide	Some	4003-130
Zinc Oxide	Considerable	4003-150
Timonox	Some	4003-152
Lithopone (Penolith EL)	Slight	4003-160
Blanc Fixé	Considerable	4003-161

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Extender	Increase in Transparency	Reference
Barytes	Considerable	JLNB 4003-173
Calcium Carbonate (Precipitated Chalk)	Some	4003-174

(B) Monochloro CPC Co-Milled at 1:3 Ratio With the Following Extenders:

Extender	Increase in Transparency	Reference	
Aluminum Hydrate	Considerable	JLNB 4077-61;	MDD-498
Aluminum Oxide	Some	4077-62	499
Zinc Oxide	Considerable	4077-60	497
Timonox	Some	4077-68	500
Lithopone (Ponolith EL)	Some	4077-69	501
Blanc Fixé	Slight	4077-70	502
Barytes	Some	4077-71	503
Calcium Carbonate (Precipitated chalk)	Slight	4077-72	504
Asbestine	Some	4077-73	505
Ground Limestone	Considerable	4077-111	
Magnesium Oxide	Considerable	4077-110	

(C) Polychloro CPC Co-Milled at 1:3 Ratio with the Following Extenders:

Extender	Increase in Transparency	References
Zinc Oxide	Considerable	JLNB 4077-147
Timonox	Considerable	4077-148

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The co-milled mixtures, when ground into paint and applied to panels, appeared much stronger than corresponding mixtures of the two constituents, because of the increased transparency. The co-milled mixtures, when ground on an ink mill, were usually very much jetter in massstone and very weak in tints. This weakness was apparently due to the fact that the extender had not been extracted. If this was done and the extracted extender replaced mechanically during the ink mill grind, the full strength of the "Monastral" pigment was developed. See JLNB-4077-111. Apparently the salt milling which follows the milling is an essential part of this type of grinding. An attempt was made to prepare a cheap printing ink pigment by co-milling CPC Crude E with wood rosin, in the absence of other grinding assistants. It was hoped that the rosin would dissolve in the printing ink during the grinding and release the full strength of the pigment. This proved not to be the case; the ink prepared was very jet in massstone and very weak in tint. See JLNB 4077-173.

Part Three - Milling Mixtures of Phthalocyanines, Other Pigments and Titanium Dioxide

A number of salt millings and ball millings were carried out on mixtures of various phthalocyanines, other organic pigments and titanium dioxide. These experiments had two purposes: First, to determine what sort of color range could be achieved by this method; and second, to guide the course of attempts to obtain analogous mixed pigments by co-baking methods. The earliest co-baking experiments showed that most organic pigments were deteriorated by the reaction conditions of the baking process. The analogous salt millings were carried out to determine whether which co-bakes were worth trying.

The following mixtures were tested by the co-milling method.

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In another series of experiments, Pigment BX-CR, or an analogous 1:1 co-bake of Monochloro CPC on "Ti-Pure" R-610 (according to the requirements of the desired ratio of blue pigment to the shading pigment) was co-milled for the usual period. An effort was made to mix the co-baked pigment, added pigment and added TiO_2 in such proportions as to duplicate the mixed pigments described in the last section, which were made by blending Monochloro CPC Crude E, the same organic pigments and TiO_2. Since the true CPC content of Pigment BX-CR was not known at the time, the checks were not good. In the table below, which summarizes these experiments, the desired blend, rather than the one actually obtained, is indicated.

Pigment	Monochloro CPC/ Pigment/TiO_2 Ratio	Mixed Pigment	References	
Ponsol Violet 4RN	1.0/0.1/3.0	Similar to Blue BX	JLNB 4077-97	MDD
Ponsol Violet 4RN	1.0/0.25/3.0	Similar to Blue 2R	4077-101	559
Helio Fast Pink	1.0/1.1/3.0	V.green vs. Blue 2R	4077-139	
Iso-dibenzanthrone	1.0/0.27/3.0	Similar to Blue 2R	4077-138	
Violet DX	1.0/0.28/3.0	Reddish-Blue	4077-96	560
Lithosol Fast Yellow HL Pdr.	1/2/3	Attractive green	4077-159	577
Lithosol Yellow G Conc.	1/2/3	Attractive green	4077-158	576
Lithosol Red 2B	1.0/0.25/3.75	Similar to 2R	4077-141	
Nickel Dimethyl-Glyoxime	1.0/0.33/4	Similar to 2R	4077-140	

Part Four - Co-Milling CPC with Colored Inorganic Extenders

In attempts to prepare cheap paint pigments, crude CPC, Monochloro CPC and Pigment BX-CR (or an analogous 1:1 bake) were co-milled with the colored inorganic pigments listed below. In the cases of the co-baked CPC products, the ratio given are those which were theoretically sought, not those actually obtained.

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Part Five - Salt Milling and Co-Milling Titanium Dioxide and other Prime Whites

The interesting results obtained by salt milling and ball milling CPC raised the question what would be the effect of salt milling or ball milling prime whites. Some work was done on this question. Since Orchem has no personnel to evaluate such products, they were sent to Baltimore for test. No reports on these samples have been returned to date. The samples submitted were the following:

"Ti-Pure" R-610, salt milled for 48 hours in a 3-gallon ball mill; extracted with 2% hydrochloric acid. JLNB 4169-45-A. Submitted to the Pigments Department, Newark, N. J., as MDD-641.

"Ti-Pure" FF, salt milled for 48 hours in a 3-gallon ball mill; extracted with 2% hydrochloric acid. JLNB 4018-137. Submitted to the Pigments Department, Newark, N. J., as MDD-608.

"Ti-Pure" R-LL, salt milled for 12 hours with 4 parts of salt in a 50-gallon mill in the Semi-Works. The salt-TiO_2 mixture was submitted to the Pigments Department, Newport, Delaware, without extraction. JLNB 4259, p. 640.

"Ti-Pure" R-LL, salt milled for 24 hours with 4 parts of salt in a 50-gallon mill in the Semi-Works. The salt-TiO_2 mixture was submitted to the Pigments Department, Newport, Delaware, without extraction. JLNB 4259, p. 64-C.

"Ti-Pure" R-LL, salt milled for 36 hours with 4 parts of salt in a 50-gallon mill in the Semi-Works. The salt-TiO_2 mixture was submitted to the Pigments Department, Newport, Delaware, without extraction. JLNB 4259, p. 64-A and B.

"Ti-Pure" R-610, co-milled with zinc oxide in a quart can. Not extracted. Submitted as MDD-588. JLNB 4077-135.

"Ti-Pure" R-610, co-milled with aluminum hydroxide in a quart can. Not extracted. Submitted as MDD-589. JLNB 4077-136.

"Ti-Pure" R-LL co-milled with zinc oxide in a quart can. Not extracted. Submitted as MDD-587. JLNB 4077-124.

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"Ti-Pure" R-LL co-milled with aluminum hydroxide in a quart can. Not extracted. Submitted as MDD-590. JLNB 4077-146.

"Ti-Pure" R-LL co-milled with Timonox in a quart can. Not extracted. Not submitted to Baltimore.

"Ti-Pure" FF co-milled with zinc oxide in a quart can. Not extracted. Submitted as MDD-586. JLNB 4077-123.

Zinc Oxide, milled alone (no salt). This sample was not submitted to Baltimore.

A mechanical mix of "Monastral" Fast Blue BX and ordinary zinc oxide (A), a mechanical mix of "Monastral" Fast Blue BX and the above described zinc oxide (B), and a co-milled mixture of zinc oxide and Monochloro CPC Crude E (C) were ground in VC-810 vehicle and compared, with the following results (Technical Laboratory Memo 523, 3-18-43)

A. Standard.

B. Sl. darker, trace greener, sl. stronger on reduction. The sample was intermediate in depth of masstone between A and C.

C. Much darker, sl. redder, cons. duller; much weaker on reduction. See JLNB 4077, pp. 60,63.

Part Six - Co-Milling Prime Whites Other Than TiO_2 With Inorganic Pigments

A few experiments were made in which common inorganic pigments were co-milled with prime whites other than TiO_2, in order to determine whether the co-milling procedure produced any new or surprising properties. Preliminary examinations showed that such co-milled products differed from mechanical mixtures of the same ingredients only in the increased jetness which has been discussed above. The results did not justify any further study of the idea.

The following combinations were tested:

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Combination	Ratio	Results	Reference JLNB
Carbon Black:Zinc Oxide	1:9	Blacker, jetter	4077-107
Lead Chromate:Zinc Oxide	1:3	Greener, duller, sl.greater gloss	4077-108
Red Iron Oxide:Zinc Oxide	1:3	Yellower, duller	4077-109

References:

Jackson Laboratory Notebooks 3865, 4003, 4077, 4139 and 4259.

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U.S. 2,212,924 (Meuhlbauer)

Lang and Detrick Case 2

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