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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Final Report

CPC GREEN MILLING AND FINISHING (LABORATORY AND SEMI-WORKS)

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NEWARK PLANT

CHEMICAL DIVISION - COLORS

Final Report

TITLE: CPC GREEN MILLING AND FINISHING (LABORATORY AND SEMI-WORKS)

PERIOD COVERED: JUNE, 1949 - MARCH, 1951

CHARGE: A-I-C-18

SUBMITTED BY: P.H. GRISWOLD/O.J.C. KLEIN DATE SUBMITTED: April 6, 1954

APPROVED BY : J. H. COOPER 7/8/54 DATE ISSUED: July 8, 1954

INTRODUCTION:

Between June, 1949, and March, 1951, several investigations on the finishing of CPC Green were made in the laboratory and Semi-works. This report summarizes this work, which was largely concerned with texture treatments, solvent milling, dispersion milling, and extraction.

SUMMARY AND CONCLUSIONS:

The principal findings and conclusions reached as results of the several studies are listed below:

A. Texture Treatments

Ink mill properties almost equal to those of GT-486-D, lot 168, are obtainable by treatment of solvent milled CPC Green (N-624) in the draft-tube, with 5% of carbon tetrachloride and 2% triethanolamine C_{12} ester. N-624 derived from either sulfur chloride or eutectic crude is suitable. A decrease in strength accompanies the treatment.

B. Solvent Milling

(1) Alkaline materials were found to be effective in inhibiting deterioration of color during solvent milling. Trisodium phosphate was the preferred material.

(2) Sodium nitrite is superior to sodium chromate as an oxidizing agent to inhibit color deterioration during solvent milling.

(3) Plant mills, the 200 gallon Semi-works mill, and the 1.8 gallon laboratory mills gave similar rates of strength development during milling. The Semi-works 58 gallon mill and the laboratory 0.65 gallon mills likewise gave equal performance, but slightly faster than the others. Eight-ounce jars were the slowest of all.

(4) Eutectic process crude behaves essentially like sulfur chloride process crude in rate of strength development during solvent milling.

C. Dispersion Milling

(1) Dispersion milling gives yellower products than solvent milling, regardless of whether the crude is derived from eutectic process, sulfur chloride process, or dry chlorination process.

(2) Dispersion milling gives products of improved texture and excellent ink mill behavior without special soft-powder treatments.

(3) The presence of "Span 80" in dispersion milling improves vinyl dispersion, but not strength or intensity by rubout.

D. Extraction

(1) "Triton" X-100 was found to be the best agent for promoting the wetting of rotating dryer crude in the extraction step.

(2) Laboratory study showed no oxidizing agent to be superior to sodium chromate in extractions of still slurries, but that chromate itself was harmful to quality.

(3) In Semi-works extractions of still slurries from Newport, it was found that:

(a) Chromate should be omitted from acid extractions.
(b) Acid concentrations below 5% are effective.
(c) NaOH is equivalent to NH_4OH in alkaline extractions.

DISCUSSION:

A. Texture Treatments

The lots comprising the Semi-works study on texture improvement are listed under "References" at the end of the report. The overall results are reported in KN-53-1 (New Draft-Tube Processing Methods), although the Semi-works lots are not referred to there specifically by lot number.

All the lots enumerated in the "References" represent variations in the technique of adding an agent in the draft-tube, such as determining the effects of heat, cycle time, point of addition, amount of agent, etc.

B. Solvent Milling

(1) Laboratory Studies

(a) Inhibition of Deterioration

Various agents were introduced into laboratory half-pint grinds to reduce deterioration in quality, because it had been shown (1348-50) that such deterioration was worse in steel mills than in glass.

A crude CPC Green which contains any residual acid material from SCl_2 chlorination not removed by extraction is most probably deteriorated during the milling operation by the reducing action of nascent hydrogen evolved in the reaction of the acidic material with the steel shot in the mill. To prevent this deterioration a laboratory milling study was made in which materials were introduced to:

(1) Remove any nascent hydrogen formed.
(2) Prevent iron from reacting with acid by complexing its ions or
(3) Keep iron from going into solution.
(4) Maintain an oxidizing medium.
(5) Maintain an alkaline medium.

Materials introduced:

(1) To remove hydrogen were nitrobenzene, benzaldehyde, quinhydrone, chloranil and quinone.
(2) To keep iron from reacting by complexing it: sodium ferrocyanide and sodium cyanide, and
(3) To keep iron from going into solution: zinc, aluminum or magnesium metal, all elements higher than iron in the electromotive series. (1348-53).

No beneficial effects were observed from addition of any of the above to the mill charges.

Materials introduced to maintain an oxidizing medium were potassium permanganate, sodium chromate and sodium nitrite. The permanganate was reduced during grinding, thus becoming ineffective. Sodium nitrite gave very satisfactory results and sodium chromate slightly poorer (1348-43, 58).

Materials introduced to maintain an alkaline medium and thereby neutralize residual acid in the crude CPC Green were zinc oxide, alumina hydrate, sodium carbonate, disodium hydrogen phosphate, trisodium phosphate. The addition of an alkaline material had a decidedly beneficial effect, with trisodium phosphate the best (1348-50, 56, 58, 62, 65, 66, 70, 71).

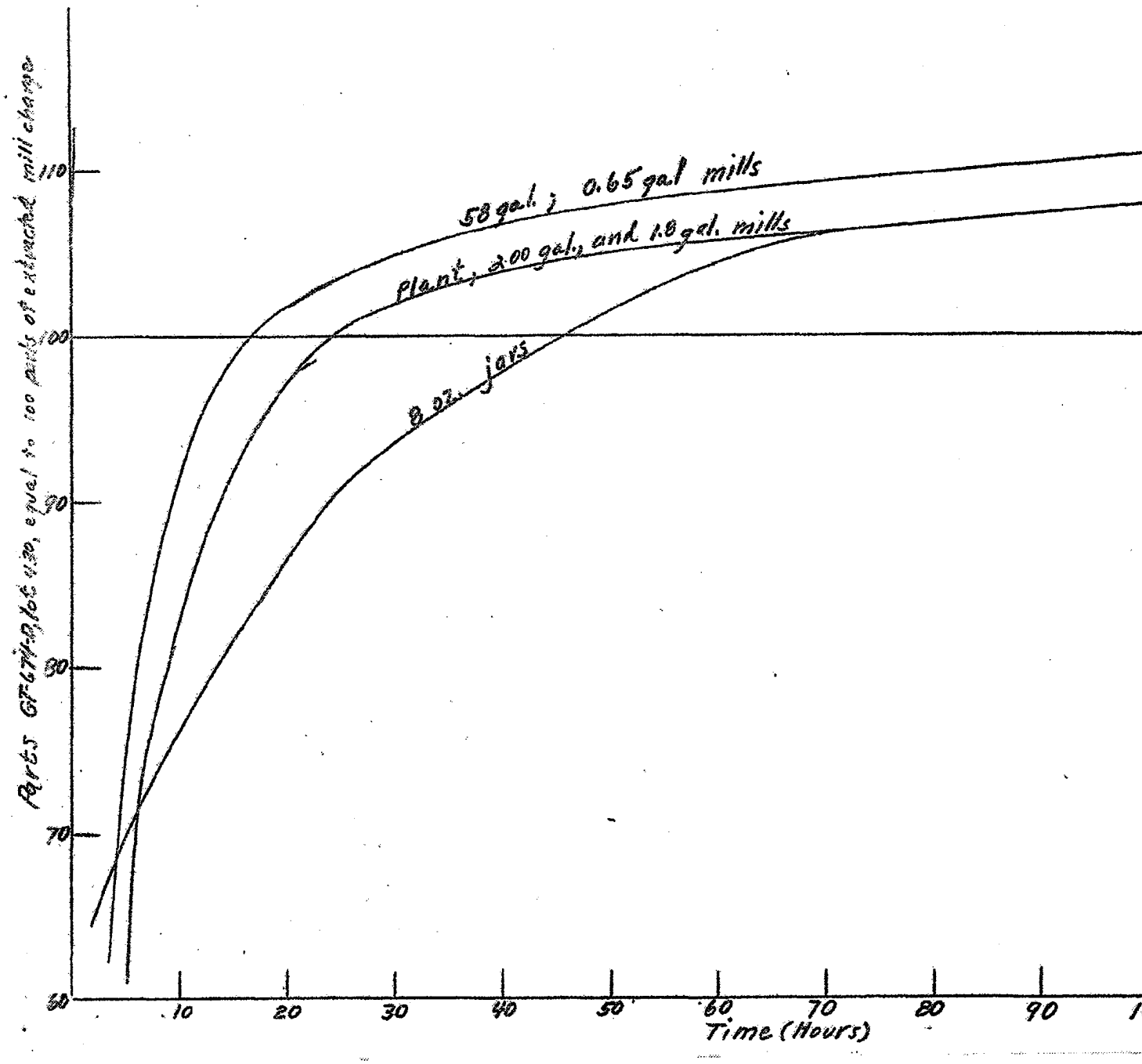
To determine whether any sulfur, which might remain with the green from SCl_2 hydrolysis during aqueous extraction, would be harmful during grinds, sulfur was also introduced in a grind. No deleterious effect was observed (1348-36, 37).

(b) Rate of Milling

A comparison of the various types of mills used for acetone milling was made in the plant, Semi-works, and laboratory. Grinds were continued for 120 hours in a 1200 gallon plant mill, 200 gallon & 58 gallon Semi-works mills, 1.8 gallon and .65 gallon laboratory mills, and 8-ounce glass jars.

The grinding curves (see graph) (strength vs. time) of the 1200 gallon, 200 gallon, and 1.8 gallon mills were practically identical. The grinding curves of the 58 gallon and 1.8 gallon mills were likewise practically identical. The 8-ounce jars were completely different from all the others, and very slow.

The color characteristics appeared to be the same at the same strength level regardless of mill size. The particular lots of sulfur chloride crude used were vs dull and vs blue at the strength level of GF-674-D, lot 430. Further grinding gave considerably more intensity, more blueness and a small increase in strength.



(2) Semi-works Studies

In the Semi-works, solvent millings were made for the study on rate of milling as described in the section on laboratory work. In addition, evaluations were made of the relative merits of sodium nitrite and sodium chromate additions to solvent millings, and of the response of "Orchem" eutectic process crude to solvent milling. Lot numbers are listed under "References".

(a) Evaluation of nitrite and chromate

The evaluation of nitrite and chromate was done in three acetone millings of a sulfur chloride process crude: a control containing chromate, a second with nitrite instead of chromate, and a third with nitrite using re-extracted crude. Use of nitrite gave a product vvs strong, intense, vs yellow versus the control. Re-extraction of the crude gave no significant improvement.

(b) Solvent Milling of Eutectic Process Crude

In studying the response of eutectic process crude to solvent milling, only the 200 gallon, 58 gallon, and 1.8 gallon mills were used. Milling was continued for 120 hours. Grinding of the eutectic green compared favorably with that of the sulfur chloride material. The strength in both cases was equal to GT-674-D, lot 430 at 24 hrs. in the 200 gallon mill, and at 18 hrs. in the 58 gallon mill. The eutectic green showed an initially higher rate of strength development, but the sulfur chloride green reached a slightly higher ultimate strength after the 120 hrs. grinding time. The masstone of eutectic green equaled that of GT-674-D, lot 430 much sooner than the sulfur chloride green, being equal at 12 hrs. and 6 hrs. in the 200 gallon and 58 gallon mills respectively. The masstone after 120 hrs. was very jet.

C. Salt and Dispersion Milling

In several Semi-works series, salt millings and dispersion millings were carried out on eutectic process, dry chlorination process, and sulfur chloride process crudes. Control solvent millings were made either in 1.8 gallon or 58 gallon mills. (See Semi-works and laboratory references for lot numbers of millings and experiment numbers of evaluations). The results are given in the section on "Summary and Conclusions".

Inconclusive results were obtained from the dispersion millings of a sulfur chloride process crude from Newport and of a eutectic process crude from "Orchem", because of deterioration during extraction. The deterioration is believed due to the presence during acid extraction of flake iron in excessive quantity. The origin of the flake iron is attributed to faster than normal wear from a charge of new "Cyl-pebs" used in the millings.

D. Extraction

(1) Laboratory Studies

(a) Wetting Agents

Turkey Red Oil, used as a wetting agent for crude extraction, was found to have a harmful effect on ultimate pigment quality. Laboratory investigation led to the following conclusions: increasing amounts caused greater deterioration (1348-60); insufficient removal by washing was harmful (1348-61); and complete elimination of Turkey Red Oil gave much improved quality (1348-62).

The following were examined in the laboratory as wetting agents:

Name	Chemical Character	Source
Colloidal HX	Soya lecithen	American Lecithen Co.
Alkanol WXN	Sodium hydrocarbon sulfonate	Orchem
Triton B-25	Polyether alcohol	Rohm & Haas
Sotex C	Condensate product of fatty acid	Synthetic Chemicals
Victamet 12	$R\text{-}O\text{-}P(OR_1)_2O$	Victor Chemical Works
Tetradecylamine acetate	- - - -	Armour & Co.
Triton N-100	Octylphenyl polyglycol ether	Rohm & Haas
Ammonyx OO	Oleyldimethylamine oxide	Onyx Oil & Chemical Co.
Glyceryl Monoricinoleate	- - - -	C. P. Hall Co.
Span 20	Sorbitan monolaurate	Atlas Powder Co.
Lissapol N	Oleic acid chloride + p-anisidine-o-sulfonic acid reaction product as sodium salt	I.C.I.
Cetyl pyridinium bromide	- - - -	William S. Merrell Co.
Triton X-45	Polyether alcohol-short ether chain	Rohm & Haas

The best of these was Triton N-100, which gave good wetting, minimum foaming and no deterioration in the finishing of the green.

When iron was present during the chlorination, extraction of the crude with acid gave improvement in quality of the final product (1348-35). Strong HCl proved to be a good acid for extraction of crude (1348-40).

Addition of oxidizing agents to crude extractions was tried as a means of improving quality. Potassium permanganate and sodium hypochlorite gave products superior to a control (1348-48).

In one experiment on acid extraction after milling, it appeared that elimination of chromate gave an improved product (1348-22).

(2) Semi-works Studies

(a) Extraction of Still Slurries

Several semi-works series were run to determine the causes of weakness in plant lots. Various combinations of acid extraction at different concentrations, with and without the presence of sodium chromate, and with or without previous or subsequent caustic soda or ammonia extraction were carried out. The results are summarized as follows:

I. Filtration of the still slurry, with no extraction; 3% H_2SO_4 extraction of the still slurry; NH_4OH extraction of the still slurry; NH_4OH extraction of the still slurry followed by 3% H_2SO_4 extraction (no chromate) - all gave products essentially equal in quality and all were vs blue and dull compared to GT-674-D, lot 430.

II. All acid extractions containing chromate resulted in significantly weaker products than corresponding controls extracted without chromate.

III. There was no significant difference between products extracted with 1%, 3% and 5% H_2SO_4 (no chromate).

IV. An ammonia extraction followed by an acid chromate extraction is equal to the reverse procedure.

V. An acid extraction following an ammonia extraction offered no quality improvement.

VI. The comparison of NaOH and NH_4OH in the alkaline extractions disclosed no significant quality differences.

VII. The masstones of all products were lighter than that of lot 430.

VIII. The fewer the number of extractions, the darker the masstone.

IX. Masstones of products extracted with acid chromate were invariably lighter than those without chromate.

REFERENCES

I. Semi-works Lots

A. Texture Treatments

(1) Draft-tube treatments
Lots 2037, 2038, 2043, 2046, 2047, 2059, 2060, 2062, 2063, 2064, 2065, 2066, 2068, 2096, 2097, 2101, 2103, 2104, 2107, 2109, 2257.

B. Solvent Milling

(1) Substitution of nitrite for chromate, 200 gallon mill grinds.
Lots 2562, 2563, 2564.

(2) Rate of grind study.
Lots 2572, 2573.

(3) Solvent milling of eutectic crude.
Lots 2606, 2607.

C. Dispersion Milling

(1) Salt and dispersion millings of eutectic process crudes.
Lots 2211, 2212, 2213.

(2) Salt and dispersion millings of sulfur chloride process crudes.
Lots 2214, 2215, 2222, 2225, 2226.

(3) Dispersion millings of four lots of eutectic process crude.
Lots 2262, 2263, 2264, 2265.

(4) Solvent milled controls to lots in (3) above.
Lots 2258, 2259, 2260, 2261.

(5) Dispersion milling and solvent milled control of dry chlorinated crude.
Lots 2302, 2303.

(6) Dispersion millings of sulfur chloride process crudes.
Lots 2582, 2585.

(7) Dispersion milling of eutectic process crude.
Lot 2608.

D. Extraction

(1) Extraction of Newport still slurries.
Lots 2503, 2504, 2505, 2506, 2507, 2508.

(2) Extractions of five different still slurries from Newport.
Lots 2530, 2531, 2532, 2533, 2534.

II. Laboratory Experiments

A. Texture Treatments

Reported in KN-50-4.

B. Solvent Milling

(1) Rate of grind study on sulfur chloride process crude.
Notebook 1367, Experiments 39, 40, 41, 43, 47, 48, 49.

(2) Rate of grind study on eutectic process crude
Notebook 1367, Experiments 56, 57, 58.

(3) Inhibition of Deterioration
Notebook 1348, Experiments 36, 43, 50, 53, 56, 57, 58, 62, 65, 66, 70, 71.

C. Dispersion Milling

(1) Evaluation of Semi-works lots of salt and dispersion millings.
Notebook 1336, Experiment 69.

(2) Evaluation of Semi-works comparisons of solvent and dispersion millings.
Notebook 1367, Experiment 7.

(3) Evaluation of Semi-works solvent and dispersion millings.
Notebook 1367, Experiment 9.

D. Extraction

(1) Trials of wetting agents.
Notebook 1348, Experiments 60, 61, 62, 67.

(2) Acid extraction of iron containing crudes.
Notebook 1348, Experiments 35, 40.

(3) Evaluation of oxidising agents in extraction.
Notebook 1348, Experiments 22, 48.