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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

CHROME GREENS
STRENGTH IMPROVEMENT - "550" LINE
LABORATORY STUDY

Period Covered: May 1947 - Jan. 1948

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Progress Report

Title: Chrome Greens
Strength Improvement - "550" Line
Laboratory Study

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INTRODUCTION

This will summarize the experimental work carried out in the laboratory during the latter part of 1947 with the object of developing blue tint greens stronger than our present "550" line.

SUMMARY & CONCLUSIONS

Recent samples of competitive greens, notably Imperial's "Vale Greens" are definitely stronger than our products. As a specific example, C#50256 (Imperial A-4442) blended with blue to approximately equal masstone depth was read as vs yellow, slightly dull in masstone vs G-550-D and strong and slightly yellow in tint. (100 parts C# plus blue was slightly strong vs 115 parts G-550-D. Reference #1263-68). The yellowness of tint was much less than that of our "604" line and attempts to improve tinting strength by adding the latter were unsuccessful.

Some years ago, we had a line of strong blue tint greens (G-503-D, G-504-D, etc.) which are now obsolete. Retained samples were examined but were found to be very olive; obviously, they had flopped on storage. Old exhibits indicate that their strength advantage would probably be insufficient to match the present competitive products.

Current production of the "550" line has run stronger than standard but only in the neighborhood of 5% (Reference 1263-52).

Experimental work was limited for the most part to a study of the yellow component, of the green, tests being made by mulling the latter with varnish drier and blue (B-216-D) paste. A few other blues were investigated briefly but none appeared to offer any advantage. Some further work along this line would be desirable. Yellows made by the standard Y-493-D procedure, (K-2009, K-2448) gave greens which were bluer than standard in masstone, more intense in tint and about equal in strength and lightfastness. Increasing the bichromate (with or without adjusting the soda ash) gave a more yellow (olive) masstone but no very significant increase in strength.

A closer match to standard Y-493-D was obtained by a modified (simplified) procedure similar to those under investigation in connection with continuous manufacture and most variable studies were made on formulas of this type. Attempts to increase strength by changes that might be expected to increase the lead chromate content of the yellow or to decrease particle size were only partly successful. The resulting products gave greens which were generally too yellow (olive) in masstone at the desired depth or too yellow in tint. More promising results were obtained by striking at a slightly elevated temperature or by the simultaneous addition of lead nitrate and bichromate to a soda ash solution. These modifications gave greens which were light in masstone and approximately equal in tint (equal blue content); with additional blue, fairly strong (ca. 110/100) blue-tint greens were obtained. These represent the most promising results obtained in the present study.

Some attention was given to a formula based on that of the strong lemon yellow Y-318-D. The latter is much worse in lightfastness than Y-493-D but by adding stannous chloride prior to the final pH adjustment, the lightfastness is improved to approximately that of Y-493-D. This procedure appears to give a slight strength advantage over Y-493-D but the (green) masstone is somewhat dull.

Attempts to replace stannous chloride with other materials were unsuccessful. Various chemicals appear equally effective in their restraining action but none gave products of satisfactory lightfastness.

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DETAILED DISCUSSION

As indicated above, most of the work was based on a simplified Y-493-D procedure. A comparison of various experimental formulas with the latter is given in the appendix.

Y-493-D Formula

The yellows obtained by both the K-2009 and K-2448 formulas gave greens bluer and more intense than standard and which were much alike in color. The K-2448 formula (low tin) gave v.s. worse lightfastness. Increasing the bichromate gave a slightly lighter and yellower masstone and very slightly duller tint. Judging from past experience, this variable must be used with caution to avoid excessive reddening of the yellow. Increasing the strike temperature (75° - 90°F) gave a lighter masstone with very little change in tint. Variations in soda ash had very little effect in the range studied.

Simplified Formulas

These differed from Y-493-D in that all the tin was added immediately after the strike; this was followed by the other ingredients without an intermediate washing step. In one modification (1263-66D, F), tin crystals, soda ash, sodium sulfide and alum are added in turn followed by more soda ash to bring the slurry to a definite pH. A further simplification (1263-66E, G) comprised simply adding tin crystals, alum and soda ash in turn. (F & G employed slightly more bichromate than D and E). Tinctorial results were much alike with the four formulas but the yellows made without sodium sulfide were very slightly worse in lightfastness. The simplified formulas gave products closer to standard Y-493-D than when the standard procedure was used, i.e. the greens were yellower (more olive).

A considerable number of experimental series were run to determine the effect of strike variables on color and especially tinting strength. Fadeometer tests were run on most samples. In general, the results in respect to strength improvement were negative. The only leads were:

a) the use of a slightly elevated strike temperature (See Y-493-D above) and
b) the use of a simultaneous strike procedure as discussed below.

Both of these modifications gave light masstone greens with little change in tint; additional blue gave stronger, blue tint material. Variables aimed at increased lead chromate content or decreased particle size usually resulted in yellow (olive) masstones and/or yellow tints. Results of miscellaneous experiments are indicated below: -

1. Omitting salt gave very olive products. Variations in the amount did not give any clear-cut effect; the standard quantity appeared to be satisfactory (Ref. 1263-8, 19, 44). Adding the salt before or after the strike offered no advantage (1263-27).

2. Replacing bichromate with chromate, i.e. precipitating at a relatively high pH gave dark masstone greens. A low pH is apparently necessary to obtain the light masstone (blue tint) type. (Ref. 1263-14, 15, 17, 23, 32, 36, 49).

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3. The final pH before flooding was apparently not critical. In general, the slurries were adjusted to pH 6.0 (Ref. 1263-2, 54).

4. High dilutions gave somewhat bluer and very slightly stronger products (Ref. 1263-20, 47).

5. Addition of sodium acetate to the lead nitrate gave very dark masstone greens. This variable should be studied further in any future work on products of the latter type, especially those based on the 1033-72 procedure (Ref. 1263-17, 19).

6. Variations in the amount of bichromate altered the masstone more than the tint. Large amounts gave yellow products and vice versa. Too high an amount gave unstable products (Ref. 1263-24, 25, 26, 32, 33, 35, 40).

7. Reducing the amount of alum gave some improvement in strength but at the expense of lightfastness. Replacing the alum with "L" Liquor or sulfuric acid had the same effect. The point of addition of alum does not seem critical. (Ref. 1263-25, 38, 40, 71).

8. Because of its well known effect on surface properties and its "restraining" action, a number of samples were made using sodium pyrophosphate in various ways. There were some indications that this gave a slight strength improvement but the results were not clearcut and, in most cases, lightfastness was affected adversely. Addition after the tin or after the alum appeared least harmful (Ref. 1263-21, 23, 26, 29, 46).

9. Increasing the amount of stannous chloride (to more than 8 grams per mole) or adding it during washing had very little effect. Stepwise addition during the strike likewise showed no advantage. Added to the lead nitrate and thus present throughout the strike, it had a powerful restraining action giving bluish greens of poor lightfastness. (Ref. 1263-25, 26, 29, 30, 31, 33, 49, 50).

10. Small variations in soda ash (added to the lead nitrate) were without any clearcut effect. Omitting it entirely and striking with chromate instead of bichromate gave a dark masstone, (yellow tint) green. Too high an amount results in a "flop". Replacement with caustic resulted in worse lightfastness. (Ref. 1263-22, 23, 24, 40, 41).

11. The presence of a small amount of sodium sulfate in the bichromate appears desirable to prevent oliveness. Too large an amount results in a flop (Ref. 1263-28, 40).

Modified Y-318-D Procedure

It was observed that Y-318-D gave greens similar in color to those made from Y-493-D but somewhat stronger. Lightfastness was much worse but could be greatly improved by adding stannous chloride after the zinc sulfate (See Appendix) prior to the final pH adjustment with soda ash. Heat development was found to be unnecessary. A number of variables were studied on this formula (1263-66A) but the work was dropped as the greens obtained were duller in masstone than those made with Y-493-D or modifications of the latter (Ref. 1263-42, 43, 45, 53, 54, 55, 58, 59, 60).

Simultaneous Strike

In veiw of the favorable results frequently obtained by precipitating chromate pigments at high dilutions, several experiments were run in which the bichromate and lead were added from separate funnels to a sodium carbonate solution, keeping the lead in excess throughout and following with the usual treating agents. This technique was tried out with several basic formulas and in all cases the yellows obtained gave greens which were definitely lighter in masstone than the controls at equal blue content and approximately equal tint (Ref. 1263-48, 49, 59, 60, 63, 67, 69). At equal masstone, they were stronger.

Comparison of Blues

Several blues were compared with B-216-D especially in respect to strength of the green which they produced. The work was limited for the most part to board mixes of dry blue and dry yellow. The blues included B-197-D, B-140-D, K-6579 (soda blue), B-63-D, B-257-D, C#-49858 (Imperial 4406) and miscellaneous experimental products. None of these appeared to offer much promise but further work is desirable, especially the preparation of "struck" greens using a slurry mixing technique (Ref. 1263-12, 18, 56).

Restraining Agents

In most of the work, stannous chloride was used as a restraining agent. Other materials gave satisfactory color but none was found giving equally satisfactory lightfastness. Sodium ferrocyanide, cuprous chloride, trivalent chromium and carboxy methyl cellulose were investigated (Ref. 1263-39, 61, 62, 65, 72).

Blending Experiments

Attempts to prepare strong products by blending "550" greens with "604" greens were not successful. Addition of the "604" type gave a yellow tint but little improvement in strength. Old samples of the obsolete "503" line (strong blue tint) were found to have flopped on storage. (Ref. 1263-13, 52).

APPENDIX

COMPARISON OF SHADING YELLOW FORMULAS

LABY. PROCEDURES (0.5 GRAM MOLE)

	Y-493-D Procedure		Simplified Procedure		Modified Y-318-D
	K-2009	K-2448	1263-66D/F	1263-66E/G	1263-66A
Lead Nitrate	165.5	165.5	165.5	165.5	165.5
Volume	3.5 l	3.5 l	3.5 l	3.5 l	5.0 l
Temperature	75°	75°	70°	70°	70°
Add to above					
Soda Ash (dissolved)	20	20	20	20	24
Strike in 20 minutes with the following dissolved together					
(Bichromate Soda	59	62	62.5/65	62.5/65	66
(Sod. Sulfate anhyd.	9	6.5	5	5	3.5
(Salt	10	10	10	10	none
(Chem. 56	none	none	none	none	0.6
Volume (strike temp)	300 cc	300 cc	500 cc	500 cc	1000 cc
Add the following in turn					
Chem. 56	none	none	none	none	8
Zinc Sulfate ($ZnSO_4$)	none	none	none	none	14
Tin Crystals	2	2	4	4	4
Soda Ash	5	5	8	none	none
Sod. Sulfide	0.5	0.5	0.5	none	none
Alum	2	2	12	12	none
Adjust to pH 4.6 and Wash 3 waters	yes	yes	no	no	no
Add in turn					
Alum	10	10	none	none	none
Tin Crystals	2	1	none	none	none
Soda Ash to	pH 5.0	pH 5.0	pH 6.0	pH 6.0	pH 6.8
Wash	no	no	3 waters	3 waters	2 waters
Dry at 140°F	yes	yes	yes	yes	yes

Notes: pH of Lead Nitrate Soln. ca. 4.7
pH of Bichromate adjusted to 4.7
1263-66 F & G differ from D & E in amount of bichromate used.