PIGMENT COLOR RESEARCH REPORT

DEVELOPMENT REPORT

Process for G-389-390-391-392-D

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FILE: ~~CHROME GREENS~~

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PIGMENT COLOR RESEARCH REPORT

DEVELOPMENT REPORT - PROCESS FOR G-389, 390, 391, 392-D

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FILE: CHROME GREENS 21.4
DATE: MAY-1935

INTRODUCTION

This series of greens was developed to obtain products possessing greater light stability than the Meadows line, G-207-D to G-210-D, and equal to the Imperial Glen Green line. Formulas for each shade have been standardized and are now giving consistent results in plant operation. The new greens correspond in depth to the old line with the exception of the extra light shade G-389-D which is of the same depth and brightness as G-365-D. The others are less olive in masstone and bluer in drawdown than the standards which they replace.

DESCRIPTION OF THE PROCESS

This process employs lead nitrate liquor instead of the tribasic lead acetate. It differs from the Meadows line also in having a higher final pH of strike - about 4.8 instead of 3.0 after addition of the bichromate. The final treated yellow may have a pH of 4.4 to 6.0 depending on the treatment. As a restraining agent, stannous chloride is used instead of tartaric ~~and~~ tannic acids. Other stabilizing agents as sodium sulphide and copper hydroxide are also employed.

GENERAL DISCUSSION

Laboratory Work. Laboratory development of a green to match Imperial's Glen Green A-4062 was begun in June 1933 and continued throughout 1933 and 1934. The product which it was proposed to duplicate was C#35302, equal in depth to G-207-D but much bluer in drawdown and tint and better in light stability.

A formula employing lead oxychloride from lead acetate and salt showed some promise in the laboratory but gave unstable results in the Semi Works. This formula was a modification of the Oliver Wilkins green in which litharge and hydrochloric acid are used (see Reports October 1933 to February 1934).

In March 1934, a 'green obtained from the Y-309-D yellow using stannous chloride (as a restraining agent) was found to possess good lightfastness but was chalky and weak vs. C#35302'. This green was obtained by dry mixing the yellow and blue.

Experiments during April were devoted "to increasing the stability of the formula so that yellow and blue could be slurry mixed and to developing a redder yellow for a more olive green". The former was accomplished by addition of various materials to the washed yellow and the latter by increasing the ratio of bichromate to sulphate.

Work was continued along these lines and in connection with Semi Works development throughout 1934.

Semi-Works. The laboratory formula, Exp. 384-77, the modification of Y-309-D discussed above, was given a Semi-Works trial in April 1934. This formula was set up as CW-7559 and a sample was sent to

Parlin for durability tests.

A detailed study was made in the Semi Works covering the ratio of bichromate and sulphate, type of lead nitrate liquor, amount of soda ash, in the base and in the treatment of yellow, and numerous other variables reported under Chrome Greens - Improved Lightfastness 1934.

This formula appeared to be unstable and particularly effected by batch size. In plant trials it was necessary to reduce the amount of bichromate considerably before a satisfactory product could be obtained. Inasmuch as plant operation was inconsistent, further Semi-Works study unsuccessful and durability on this product found to be inferior to competition, the problem was returned to the laboratory (September 1934).

An improved formula, Lab. Exp. 411-63C, was then tried in the Semi Works with promising results. This formula, CS-7694, differs from the preceding one in several respects, although basically it is of the same type. The chief differences are a higher strike temperature, high volume, use of sodium sulphide and of cupric hydroxide. This formula also received a thorough study in the Semi Works, the most promising results being obtained from variation in the treating agents.

Semi Works batches were brighter in masstone and slightly weaker than C#35302, the Imperial product. Light stability appears to be equal (October 1934).

Plant standardization was begun in October 1934 and in December, tentative standards for three shades (XL, M & Dk) were set up. These together with another light shade were accepted by Philadelphia and Parlin and coded as G-389-390-391-392-D in order of depth.

Plant. Production was begun in the plant in January 1935 and carried on intermittently until March at which time a regular schedule for all shades was lined up. Difficulty was experienced at first in obtaining brightness of masstones equal to the standards, and it was necessary to reduce the alkalinity of the finished yellow by omitting the soda ash from the after treatment. This gave a very definite increase in brightness of masstone and tint. Attempts were made to eliminate the use of copper hydroxide but because of instability on the dark shade green G-392-D and because of its effect on light resistance it is advisable to continue its use until complete outdoor exposure tests are available.

Stocks and Yields - Stocks of all shades have been made up. The estimated production and shipments for the first four months of 1935 are shown below.

	G-389-D	G-390-D	G-391-D	G-392-D
Production (approx.)	12000#	5500#	7800#	6800#
Shipments	3540	140	2204	753

Disregarding a few batches in which the yields are abnormally low due to losses in pressing or from fire an average yellow yield of 325# per mol is obtained.

The following amounts of blue are used, expressed as percentage of the finished green.

	G-389-D	G-390-D	G-391-D	G-392-D
% Blue (formula)	5.0	10.5	24.0	43.0
" (by analysis)	5.9	10.1	25.0	42.5

As a comparison, the figures for the Meadows line are also given:

	G-385-D	G-208-D	G-209-D	G-210-D
% Blue (formula)	5.0	8.5	21.5	36.0
" (by analysis)	4.97	7.83	21.37	34.83

The higher blue content of the G-389-D line is reflected in the bluer undertone and higher raw material cost.

Costs of G-389-D line		Costs on Meadows line	
G-389-D	9.83	G-385-D	7.01
G-390-D	10.38	G-208-D	9.28
G-391-D	13.44	G-209-D	11.80
G-392-D	16.63	G-210-D	14.86

DETAILS OF OPERATION

Materials

Lead nitrate. It is necessary to use lead nitrate liquor having little or no copper or other metals present as impurities. When sludge is used in making the liquor, the latter should be purified by circulating over sheet or feathered lead.

Soda Ash in base. Variations have been made in the plant from 98 to 104# soda ash per 2 mol charge of lead nitrate. With the lowest amount, the soluble lead at the end of bichromate addition is greater while with the highest amount the lead test is likely to be slight or almost negative. The former condition is favorable to brightness provided the resulting acidity is not too great; in the latter case (high soda ash) dullness and changeability may occur in the green.

An average of 101# soda ash appears to be a satisfactory amount. pH control of the base is not practicable as a 10% change in soda ash in either direction had no effect on the pH reading. Physical changes, such as batch size and temperature have more influence.

Variations in amount of soda ash used are reflected in different pH readings taken after the strike.

The soda ash should be dissolved.

Bichromate of Soda. The amount of bichromate of soda used in the standard formulas is 232# per 2 mol charge, sufficient to precipitate 78% of the lead. The following variations in bichromate and sulphate have been tried in the plant with results noted below.

Per 2 mol charge	I	II	III	IV
Sod. Bichromate	232	237	242	242
Sod. Sulphate in bichromate	22	16	11	22
Sod. Sulphate after bichromate	25	25	25	25

I - This is the standard ratio and usually gives a somewhat bluish masstone at all depths.

II - This gives a slightly olive masstone and is probably a safe variation to make to obtain this effect. An intermediate amount should be tried.

III - The higher ratio of bichromate while successful on several plant batches, even of the dark shades G-391-D and G-392-D, approaches the unstable point and is likely to give off material.

IV - Precipitation of the bichromate in the presence of the higher amount of sodium sulphate gave a bluer masstone than obtained by III. There is no apparent advantage to this combination as compared to I and II.

No correction for the increased acidity due to the bichromate was made in trying the above ratios. However, to balance the acidity the following additional amounts of soda ash should be used in making up the base:

I	II	III	IV
0	1-1/2	3	3

Sodium Sulphate. This should be sufficient in amount to precipitate the slight lead excess remaining after the main precipitation with bichromate-sulphate. If insufficient, the yellow is likely to be changeable as the restraining agents are less effective in the presence of soluble lead.

Amount of salt. This has not been checked in the plant, and Semi-Works results on a previous formula are inconclusive.

Tin crystals. This material acts as a restraining agent and prevents change in crystal form and consequent redness in the yellow. The amount is 33% higher than on the earlier formula CS-7559 first tried in the plant. Reduction to the lower amount has not been rechecked. It is necessary to employ it at both points as in the formula. The sodium sulphide is also believed to have some restraining action.

Alum. Addition of alum to the washed yellow preceding the tin crystals produces a brighter and more lightfast green. Use of soda ash to precipitate the alum has been discontinued as it was impossible to obtain clean masstones and tints. All but a small amount of alum appears to be precipitated probably by the basic lead carbonate remaining in the yellow.

Copper hydroxide. The employment of this reagent, while inconvenient in plant operation, appears to be necessary for stability in processing, particularly in the dark shades. In the light shades, omission of copper hydroxide has been observed to cause flatness of masstone on the dried rubout and loss of gloss on exposure in the fadeometer. The actual darkening effect is no greater however. Outdoor exposures are being made to determine the practical effect of omitting this material.

The copper hydroxide should be made up carefully in order to obtain as stable a product as possible. High temperature, concentrated

volumes, too great an alkalinity and poor agitation tend to cause the precipitate to turn black quickly. The test after adding caustic soda should be slight on Red Litmus paper.

OPERATION

Volume of strike. The volume of the lead nitrate before striking is relatively high (2400 gallons per 2 mol charge). A lower volume (960 gallons) was used on CS-7559 of which the present formula is a modification. Results on CS-7559 were not successful as to stability of color or resistance to light and there is some evidence that the difference in volume had some effect. However, if necessary, further comparisons should be made. A Semi Works batch with a 50% reduction in volume showed little tinctorial difference but did show a little decrease in light stability.

Temperature of Strike. The temperature of 110°F is probably the most suitable. It is suggested that at this point the lead chloride is kept in solution to some extent as it is formed ensuring greater stability as the strike proceeds. In the Semi Works, 120°F was unsatisfactory due to oliveness and 75°F was objectionable because of dark masstone and somewhat inferior light stability.

Time of strike. A one half hour strike has been adhered to in practically all of the plant development work. One batch struck in 12 minutes was equal to a control run. In the Semi Works it was possible to strike in 5 minutes without harmful effect provided the agitation was adequate. Increasing the time of strike to 2 hours resulted in an olive product. A uniform rate of addition of bichrome in 20 to 30 minutes is probably best adapted to plant equipment. There should be no delay in adding the sulphate and tin crystals following the bichromate.

Agitation. Good agitation is required in making this line of greens. Very poor agitation tends to give olive products of inferior light stability. 24 RPM in the 4000 gallon vats in the plant and 14 RPM in the 8000 gallons are lowest speeds which should be used, but 26 RPM and 16 to 20 RPM are recommended for most consistent results.

Batch size. No difference was observed in an increase in batch size from a 2 mol to a 4 mol charge. Provided agitation is sufficient, 5 mol charges can undoubtedly be made. A possible exception is the darkest shade, G-392-D, which has not yet been tried.

Washing. Single Semi-Works runs showed a loss in cleanliness of masstone and tint when washing was reduced from 3 to 1 water, and also when the yellow was washed, shaded and pressed out on the same day. Temperature of wash water has not been studied but there is a wide variation in this throughout the year.

Drying. No precise information was obtained on drying temperatures, but it is believed that too high a temperature (above 170°F) will reduce brightness. On the other hand, fairly rapid drying (48 hours) is desired to avoid oliveness. 160°F is probably a safe average temperature for plant operation.

Control Tests. The following tests will indicate that the charge is normal but with the exception of the test for sulphates before flooding and the final pH of the treated yellow, no adjustments are practical. The test for excess sulphates should be observed, particularly as a deficiency of sodium sulphate can produce changeability in the yellow. The lead test after strike should be observed but chiefly to make sure that no chromate is present.

(1) After bichromate
pH = 4.6-4.8 average; 4.4 and 5.0 also OK
(Bromcresol green indicator)
Lead excess - slight to positive with 10% H_2SO_4

(2) Struck yellow before flooding
pH = 5.8- 6.0 average
(Bromcresol Purple indicator)
Sulphate excess - positive test with 10% $BaCl_2$

(3) Treated Yellow
pH = 4.2 without copper hydroxide
pH = 4.8-5.0 with "
(Bromcresol green indicator)

(4) Copper hydroxide - slightly alkaline on Red Litmus paper.