NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

DEVELOPMENT REPORT - PROCESS FOR G-409, 410, 411, 412-D

December 26, 1935

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PIGMENT COLOR RESEARCH REPORT

DEVELOPMENT REPORT - PROCESS FOR G-409, 410, 411, 412-D

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INTRODUCTION

These greens compose a new yellow undertone line similar in this respect to the Milori line, G-315 to 318-D, but possessing greater light stability. The new standards correspond in depth to the G-389-D series but are less clean and bright in masstone.

Description of the Process

Tribasic lead acetate is used. An initial pH of strike of about 6.9 is obtained by addition of nitric acid. To this is added bichromate of soda equivalent to 85.5% of the lead, followed with sodium sulphate equivalent to 14% of the lead. The same stabilizing agents are employed as in the G-389-D line - stannous chloride, sodium sulphide, and copper hydroxide. The struck yellow has a pH = 5.4.

General Discussion

Laboratory Work. With the completion of the research and development work on the improved Meadows greens, laboratory work on more light fast greens of the Milori type was begun in November 1934. Two types of formulas were studied (December 1934). (1) One "process consists of the addition of sodium chromate and salt to lead nitrate followed by the restraining agent". The restraining agents used are stannous chloride and sodium sulphide." Lab. Exp. 439-24B. (2) "Milori Greens prepared from lead liquor possess good strength and light fastness when stannous chloride and sodium sulphide are used as restraining agents". The general process is to add an acid, preferably nitric acid to lead liquor and strike with bichromate. This formula, Exp. 439-56C, is a modification of the strong Milori formula, K-7728. The above processes were tried in the Semi-Works.

Semi-Works. The all chromate formula (439-24B) gave some promise but did not possess sufficient strength or the proper masstone - undertone relation for a Milori green. The modification of the strong Milori formula, Exp. 439-56C gave a very desirable product. About 10-15% stronger than G-317-D, it was much better in light stability. It is slightly bluer in tint (December 1934).

This formula was dropped in favor of the cheaper and perhaps more stable type (Exp. 436-56A or SW-6652) in which all the nitric acid added before the strike and a lower amount is employed because of the omission of caustic soda (January 1935). This was the CS-7764 type which was the basis of intensive Semi-works study during January and February 1935.

An increase in batch size from 0.1 to 0.5 mol as well as a plant trial showed a tendency towards oliveness in the larger sized batches.

A reduction in bichromate ratio together with an increase in nitric acid sufficient to maintain the acidity gave an increase in brightness with somewhat reduced lightfastness and of course less strength.

The former was corrected by addition of tin crystals directly after strike as well as after washin: the yellow (SW-6808 type). The bichromate was then increased to its original amount as in SW-6673 (K-7764) and with the tin crystals added after strike, the strength desired was regained without affecting the blueness and brightness". (February 1935).

A study of other variables of the formula was made in the Semi-works in July 1935 in order to assist in plant development.

Plant. A 2 mol plant charge on K-7764 formula was somewhat dirty in masstone (January 1935) and when development work was resumed in April, the reduced bichromate formula (SW-6808 type) was used. Shaded to the depth of G-317-D, the products obtained were slightly blue and bright in masstone with equal strength and better light stability. A repeat run on the high bichromate formula was olive and changeable.

In plant operation during May and June, progress was held up because of oliveness occurring in the lighter shades of the proposed line. This was finally eliminated by the use of proper temperature and volume of strike and improved agitation. Use of copper hydroxide was also adopted as a further stabilizing agent (July 1935).

Final standardization of the line was completed in September 1935 with production of all four shades on the basic yellow formula, K-7889. These were coded as G-409, 410, 411, 412-D.

Stocks, yields and costs - The amounts of standard color and of substandard material remaining are as follows:

G-409-D	(K-7889)	Lot 15471 - 2181#	(Extra Lt.)	Substandard =	800#
G-410-D	(K-7890)	" 15574 - 2510#	(Light)	"	none
G-411-D	(K-7992)	" 15440 - 1890#	(Medium)	"	none
G-412-D	(K-7891)	" 15451 - 2019#	(Dark)	"	445#

The yield of yellow averages 315# per mol Pb O.

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

		G-409-D	G-410-D	G-411-D	G-412-D
% Blue	(formula)	3.5	8.0	23.5	39.5%
"	(by analysis)	3.44	7.82	19.66	37.0

The figures for G-410-D are on Lot 15574 which was shaded slightly darker than K-7890 and reformulated as K-8018.

The latest blue percentages for the G-389-D line are:

		G-389-D	G-390-D	G-391-D	G-392-D
% Blue	(formula)	6.0	10.5	26.0	43.0%
"	(by analysis)	5.9	10.09	25.02	42.5

The following are cost figures for the two lines:

	XL	L	M	Dk.
G-409-D line	$8.89	9.49	12.67	15.69
G-389-D line	9.57	10.33	13.24	16.47

(These figures are based on the formula amounts of blue).

It is possible that the amounts of blue formulated in the G-409-D line are too high; revisions, if necessary. will be made after manufacturing experience is accumulated.

The following comparison of costs is on the basis of approximately equal tint. The G-409-D line is about 25% stronger and is cleaner than the G-389-D line, the difference in cleanliness being more pronounced in the light shades. Naturally the masstones of the G-409-D line are much darker.

G-410-D 95% } at $9.64 equivalent to G-389-D at $9.57
G-411@D 5% }

G-411-D at $12.67 equivalent to G-390-D 70%) at $11.20
G-391-D 30%)

G-412-D at $15.69 equivalent to G-391-D 65%) at $14.37
G-392-D 35%)

Taking into account the additional strength of the G-409-D line, it has a distinct advantage in cost for a given tint.

Details of Operation

Nitric acid. Correct acidity is important but control by pH tests is not feasible due to the buffered condition of the lead solution. A 3% variation in nitric acid is probably not harmful but greater changes (10%) in either direction cause oliveness and dullness.

Volume of strike. Although the volume of the lead in this formula is higher than ordinarily used, a reduction has not so far been successful. At a 35% lower strike volume the product was slightly olive and weak. 50% and 75% reductions gave dirty masstones and in one case a distinctly olive product.

Temperature of strike. A higher temperature than 70°F tends to cause oliveness. This is noticeable to some extent at 75°F and quite positive at 80°F.

Rate of Agitation. Reduced speed of agitation resulted in an olive slightly dirty color in the Semi-Works. Someof the early difficulty met with in the plant may have been due to insufficient agitation. When the direct driven agitators were installed, speeds of 16 and 20 RPM were found to be satisfactory on 2 and 4 mol charges made in the 8000 gallon vats.

Amount of Bichromate - Increasing the bichromate ratio from 85 to 92% of the lead (PbO) added slightly to oliveness and definitely to the strength in Semi-works runs. In the plant the higher ratio was unstable.

Sodium Sulphate in the Bichromate - On a single Semi-works run there appeared to be no advantage in co-precipitating some sodium sulphate with the bichromate. Omitting the final sodium sulphate and finishing the yellow with a lead excess increased oliveness and had no effect on light stability.

Tin Crystals. Addition of tin crystals after the bichromate as well as after washing the yellow appears to be necessary for greatest stability. It should preceed the sodium sulphide in order.

Sodium Sulphide - Omitting or reducing in amount the sodium sulphide caused poor light stability although the product obtained was lighter and cleaner. Use of a double amount had the opposite effect giving somewhat dirty olive masstones with equal or better light stability. It is believed that the sodium sulphide should be added slowly and with good agitation of the yellow. Addition of hydrochloric acid equivalent to the sodium sulphide had an effect similar to reduction of the latter.

Copper hydroxide - The stabilizing effect of this reagent on dark greens has been conclusively demonstrated. It appears to be also helpful in preventing changes during processing in light shades. It may have a slightly adverse effect on light stability.

Washing and Drying - No positive information has been obtained on these operations but they should probably be carried out as rapidly as possible.

Control Tests.

(1) The lead solution before strike has a pH of about 6.9 but this test is not sufficiently sensitive to variation in acidity to be of use.

(2) After addition of bichromate, a strong lead test should be obtained when 10% sulphuric acid is added to a filtered sample. The pH at this point is normally 5.2 - 5.4.

(3) A positive sulphate excess should be present before flooding the yellow.

(4) The yellow after treatment has a pH of 5.7