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PIGMENT COLOR RESEARCH REPORT

Final Report

SUMMARY OF LABORATORY WORK ON CONTINUOUS MANUFACTURE OF CHROME YELLOWS - (SUMMARY OF KN-44-77, 78, 79, 80, 82)

Period Covered: JULY 1, 1943 - DECEMBER 31, 1944

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SUBMITTED BY: V. Chalupski DATE SUBMITTED: 2-3-45

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This is a summary of the research reports issued in January 1945 which cover the laboratory experimental work on continuous manufacture of chrome yellows, Research Project #207, July 1, 1943 to December 31, 1944. (KN-44-77, 78, 79, 80, 82). Not included in this summary is the work done on Molybdate Orange and Zinc Yellow (KN-44-81, KN-44-83).

The manufacturing steps for making chrome yellow which requires study in connection with continuous operation are:- 1) Precipitation; 2) development - heat and ageing; 3) hydrous oxide treatment; 4) removal of soluble salts by washing.

KN-44-77

This report discusses the general aspects of the problem and describes the laboratory equipment. Earlier studies of continuous manufacture of chrome yellows were concerned only with the precipitation step. Laboratory and large scale work showed that continuous precipitation gave products similar to those made by batch predipitation. Recent work has shown that in the case of most chrome yellows, the mechanical conditions of precipitation are not critical in the sense that pigments of reasonable quality are obtained if chemical conditions and concentration and temperatures are similar to those used in batch precipitation. On the other hand, variations in color which are comparatively minor from a scientific point of view, but which may be of some commercial importance, can sometimes result from changes in mechanical conditions.

The object of the current study has been to make the manufacturing process completely continuous. This implies that each of these manufacturing steps mentioned earlier shall in themselves be carried out continuously and each step shall follow the preceding one continuously.

Preliminary laboratory experimentation was carried out batchwise. The order of the various steps was arranged to correspond to the order which would be most advantageous in continuous operation, and each step was carried out as rapidly as possible to stimulate conditions which were assumed would occur in continuous operation. However, it was realized that it is impossible to duplicate the conditions which occur in continuous manufacture by batch methods. To what extent this batch method of experimentation should be used to establish conditions before going to experimental work by the continuous method is still a moot point.

KN-44-78

This report covers the work on medium yellow Y-469-D. This is an ordinary type of medium yellow which contains only a comparatively small amount of hydrous TiO_2 and no alumina. The first problem taken up in making this a continuous process was the elimination of the decant washing step (which also undoubtedly serves as an ageing step) between

the development and hydrous oxide steps. Merely omitting the washing/ageing step results in dark masstone and poor lightfastness. A few experiments were run to determine the causes of this dark masstone. It may tentatively be concluded that neither the presence of soluble salts nor the higher temperatures of the yellow at the treating step was responsible. It was found that an ageing period of about 30 minutes could be used to replace the washing/ageing step with some measure of success, although there was a tendency toward the less desirable dark masstone.

Having eliminated the one step which made the process as a whole discontinuous, some study was given to the individual steps. Variations in mechanical conditions of the precipitation step were tried in the laboratory continuous unit. Recirculation of the precipitated slurry back thru the region where precipitation is taking place may have some little adverse effect (the term "adverse effect" as used in this discussion usually means dark masstone and poor lightfastness). Variations in the arrangement of the jets thru which the reacting solutions enter the precipitation unit appear to affect strength. Greater strength is obtained when the reacting solutions meet at the point of maximum agitation. Increasing the agitation speed also gives somewhat greater strength.

Temperature and time of heat development was also studied. Subsequent work on other colors showed that heating in two or more stages is desirable; this will be referred to again in subsequent discussion. In the study of Y-469-D, the continuous development steps appear to give somewhat weaker yellows than batch development at the same temperature.

The hydrous oxide treatment of this color consists in the addition of titanyl sulfate solution followed by the addition of a solution of sodium carbonate. These were added to the developed yellow suspension either in small agitated units or by pipe line mixing. In either case there was some deterioration in lightfastness compared to batchwise hydrous oxide treatment.

A study was also made of pH of precipitation and excesses of the reactant. The data obtained applied both to batch and continuous methods; it was found necessary to do this work because the information desired for control of the continuous preparation step was not available. Previous work has shown that a soluble chromate excess is necessary during the precipitation and development stages; its absence results in poor masstones and lightfastness. Too high an acidity also results in a poor product. If the pH of the slurry is more acid than about 5.4 after the precipitation, as it passes thru the development stage the pH will drop to 3 or below, and poor masstone and lightfastness will result. A pH of about 6 after the precipitation, with a slight chromate excess, is satisfactory. This pH will remain fairly constant during the subsequent development.

KN-44-79

Standard Y-404-D and Y-405-D processes have steps in them which do not unduly complicate batch manufacture, but which are undesirable in continuous manufacture. These are (1) addition of sodium carbonate after the strike, (2) addition of sodium sulfate after development to precipitate lead excess and (3) as in the case of the batch process for Medium Yellow Y-469-D there is a decant washing step after development, before the hydrous oxide treatment.

These were eliminated by (1) adjustment of the alkalinity of the reacting solutions so that sodium carbonate addition was unnecessary and(2) with elimination of the washing step, which was replaced by a short ageing period, the excess lead was precipitated when titanyl sulfate or aluminum sulfate was added for the hydrous oxide treatment.

An improved Light Yellow K-1957 has been developed which differs from the Y-404-D process chiefly in the use of more hydrous oxide;-

Y-404-D 1% of hydrous TiO_2
K-1957 3% of hydrous alumina plus 2.4% hydrous TiO_2

The K-1957 formula was revised, as discussed above, for continuous operation. A detailed study of the heat development step resulted in a three-stage development, the first stage to 140°F., the second to 170° and the final to 200° or boil.

Best results were obtained by adding each of the ingredients of the hydrous oxide treatment (aluminum sulfate, titanyl sulfate, sodium carbonate) separately, and in separate, well agitated small reactive vessels of the "draft tube" type.

No study of the continuous addition of the texture agent was carried out. It is planned to add this material during the centrifuging-repulp washing cycle, on the large scale.

KN-44-80

This is a progress report, already somewhat out of date. It discusses work prior to November 1944 on the laboratory development of a continuous process for a new medium yellow, K-1958, the batch process for which differs from standard Y-469-D in using more dilute solutions, higher development temperature and higher amount of hydrous oxide, like K-1957, discussed in KN-44-79. A satisfactory continuous process for K-1958 has not yet been developed.

It was found that this new medium yellow process is more difficult to convert to continuous operation than the old standard Y-469-D; all early attempts resulted in dark masstone and worse lightfastness. A phenomenon which is particularly difficult to study is the darkening of masstone as the pigment/oil mount ages and dries. Many experimental products appear equal to the goal standard when freshly drawn down, but

after the mount has dried overnight, and particularly after it has been exposed to heat (for instance, the shielded part of the mount in the fadeometer), the experimental material is very dark in masstone. This is always accompanied by apparently inferior lightfastness. A large number of formula changes were tried, most of them in a simplified batch method, which was modified in a manner similar to formulations discussed in the preceding report. These changes included eliminations of intermediate washing steps and the like. Experiments run by the batch method are discussed on pages 3 and 4 of the report and are summarized below.

1. Elimination of chromate excess after the heat development, by addition of lead nitrate gave slight improvement in masstone accompanied by loss of strength.

2. Longer ageing. Sixty minutes better than fifteen minutes.

3. Treatment with sodium silicate. No desirable effect.

4. Hydrous Oxide treatment carried out in steps. Improvement was doubtful.

5. Addition of titanyl sulfate before the alum. No effect.

6. Slower addition of sodium carbonate to precipitate the hydrous oxide. This minimizes darkening in oil.

7. Sodium fluoride present during strike (in chromate solution). About 5 grams per gram-mol of lead chromate. Better masstone and lightfastness, weaker. Sodium chloride has similar but lesser effects. Electron microscopic examination shows that these materials cause an increase in particle size.

Some laboratory work done in the continuous unit is also covered in this report. Two-stage heat development was used; material made continuously thru this development step and finished batchwise is satisfactory.

There is only a slight loss in quality caused by continuous addition of the alum but a marked deterioration with continuous addition of titanyl sulfate and sodium carbonate. Considerable study has been given to these steps, but no solution to the present difficulties has yet been found.

It was found that the aluminum sulfate is not precipitated until the pH is raised above 3.0. The titanyl sulfate hydrolizes quite rapidly even before the sodium carbonate is added, at as low a pH as 1.1.

KN-44-82

This report discusses the study of a continuous process for "shading" or "greening" yellow; i.e., a chrome yellow designed to be mixed with iron blue to make a green. Such yellows are Lead Chromate/

Sulfate mixtures or shading

Sulfate mixtures containing a comparatively small amount of sulfate. These yellows are strong and quite green in hue. They are much smaller in particle size than the ordinary light and medium yellows. Shading Yellows are usually precipitated under more acid conditions (as low as pH 2) than the light and medium yellows; immediately after precipitation, it is necessary to stabilize the very small particles formed by the addition of various so-called restraining agents, (tannic acid, tartaric acid, tin crystals, alumina hydrate), and by partial neutralization to a pH range in which crystal growth is slow. (pH from 4.5 to 6 depending on the ions present).

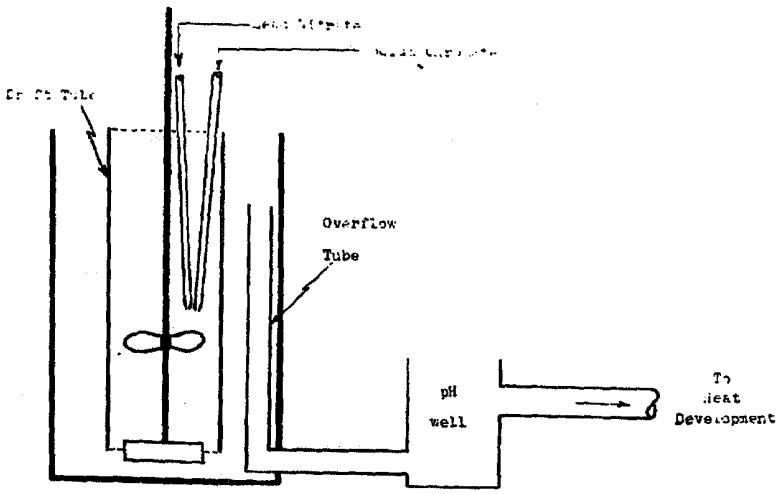
This study was based on a new batch process in which all making steps are carried out successively without any intervening washing or ageing periods. The steps in this process are as follows:-

1. Addition of Soda Ash to Lead Nitrate to form a Lead Carbonate base.
2. Addition of sodium bichromate/sodium sulfate mixture to this base to precipitate lead chromate and lead sulfate.
3. Addition of tin crystals (restraining agent).
4. Neutralization with sodium carbonate.
5. Addition of aluminum sulfate.
6. Neutralization with sodium carbonate.

Attempts were made to simplify this process further by eliminating the preliminary formation of the lead carbonate base and instead reacting lead nitrate and sodium chromate solutions directly, adjusting their acidities to give the same final acidity as in the above process. Products thus made were satisfactory in color, but were somewhat inferior in lightfastness, so this line of attack has been abandoned temporarily.

Experimental work was carried out in the laboratory by both batch and continuous methods. Mechanical conditions in the lead chromate precipitation step are much more important than in the other yellows; large tinctorial variations can be obtained by changing jet positions, agitation, etc.

A number of minor variables were studied; effects obtained agreed with previous experience with standard batch operation. At selected mechanical conditions, and with a formula not differing in any essentials from the batch process, products close to the present standard were obtained. These were satisfa ctory by rubout, paint grind, and outside exposure.



Continuous Strike Jar

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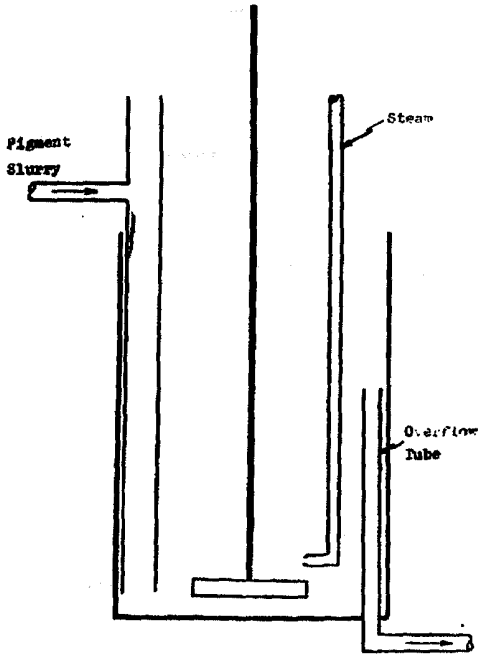
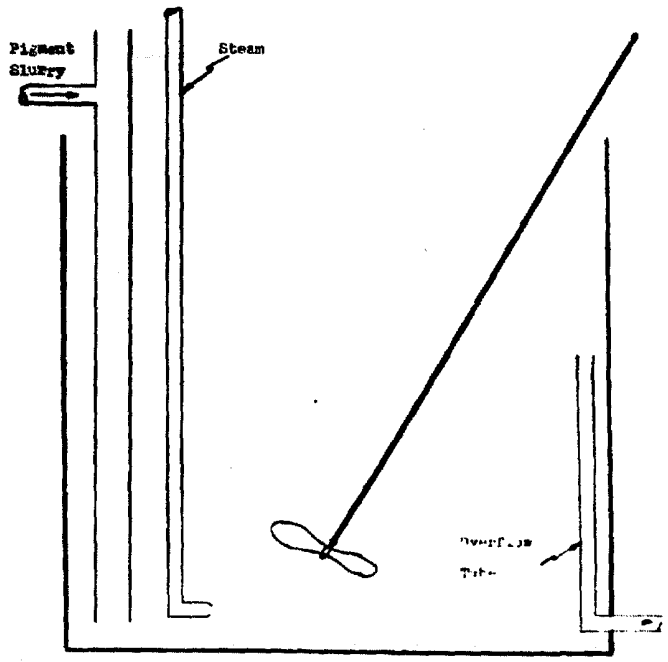


Continuous Heat Development - 160°F.



Continuous Heat Development

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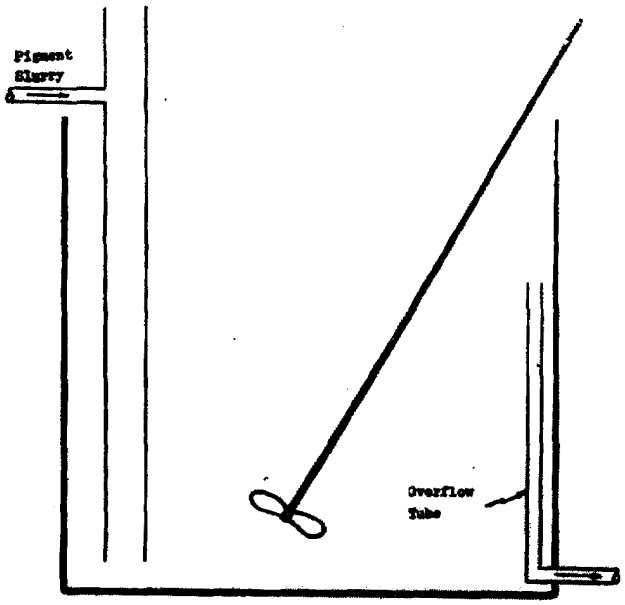
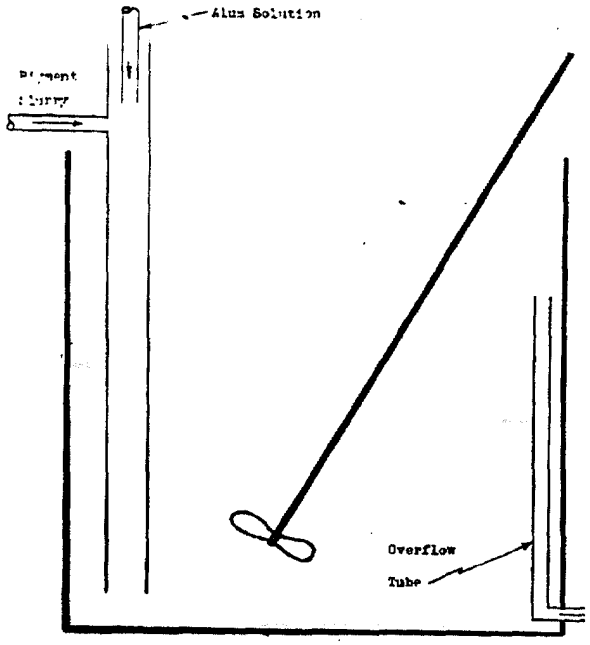


Continuous Aging Jar



Continuous Treating Jar for Alum

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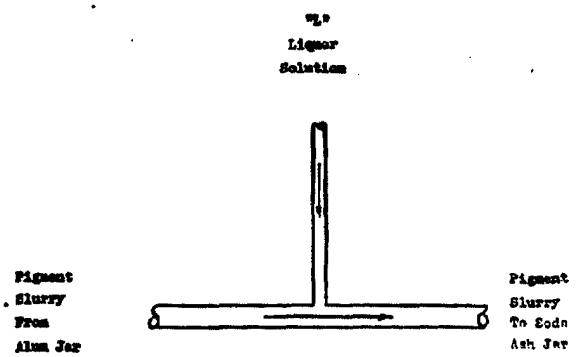
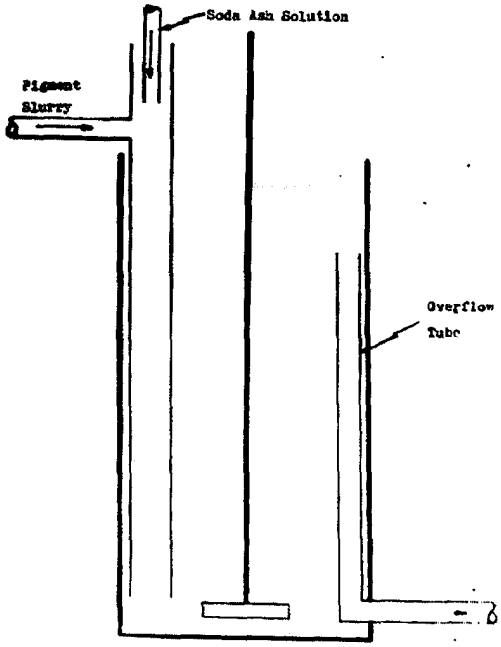


Continuous "L" Liquor Addition



Continuous Treating Jar for [illegible]