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PROJECT J-1070

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SUBJECT: DEVELOPMENT OF MORE COLOR STABLE CREAMS

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PREPARED BY: E. J. BARRETT, JR.

APPROVED BY: J. H. LOWELL

SUBJECT: DEVELOPMENT OF MORE COLOR STABLE CREAMS

INTRODUCTION

The poor color stability of cream formulation in comparison with other "Duco" colors has long been a problem. In the past, even with this disadvantage, "Duco" creams have maintained a high competitive position in the trade. Recently, however, competition has introduced creams of improved color stability presumably based on new yellow pigments. In an attempt to maintain our competitive position project J-1070 was introduced to re-examine the newer yellow pigments with the aim of finding a non-fading substitute for lead chromate, which is the unstable component of the current cream formulations.

SUMMARY AND CONCLUSIONS

Work centered on two yellow pigments on which previous exposure background indicated good color stability. They were as follows:

1. Bright Yellow "Ti-Tint", a nickel complex of titanium dioxide.

2. Lithosol Yellow, a nickel complex of p-chloraniline diazotized and coupled to 2,4 di-hydroxy quinoline.

Bright Yellow "Ti-Tint" on formulation and re-exposure showed excellent color stability and was free from color drift in the wet state; however, its tinting strength was very weak. Only very light creams could be matched with it and consequently, its usefulness as a major tinting enamel was quite limited. For those colors which could be matched with it, results were good and formulation was routine.

Lithosol Yellow seemed to have most of the desirable characteristics for creams, such as good tinting strength and excellent light fastness; however, in the nitrocellulose vehicle it changed color rapidly in the wet state. Most of the work on this project centered on attempting to overcome this defect.

Citric acid, a gelation inhibitor and viscosity stabilizer, normally used in 253 and 246-line "Duco" enamels was found to be the major cause of the color instability of Lithosol Yellow. To a lesser extent the normal acidity of the nitrocellulose vehicle was also a contributing factor.

From information uncovered on this project it has been concluded that zinc oxide, because of its alkaline nature, can be used to impart adequate wet-state color stability to Lithosol Yellow with the following procedure:

1. Lithosol Yellow tinting enamel must contain 0.5% Zinc Oxide. (This constitutes approximately 10% of the pigment).

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2. In formulations containing the above, tinting enamels containing citric acid (G-499) must be carefully restricted to 5% of the total formulation. (At present levels this amounts to a maximum of .015% citric acid).

3. A special acid-free white tinting enamel containing additional zinc oxide must be used so that the final composition will contain at least 0.35% zinc oxide.

Improved cream formulations based on Lithosol Yellow with the above formulating procedure were recommended in Parlin Laboratory Release Letter #383. Limited production approval has been granted on this release.

PATENT INFORMATION

Information disclosed by this report does not appear to involve potentially patentable material which is not already covered by pending applications or existing patents.

CONFIDENTIAL INFORMATION

The information disclosed in this report is considered to be within the scope of Schedule B of the C.I.L./du Pont agreement and not of unusually confidential nature.

EXPERIMENTAL

The Effect of Zinc Oxide On The Stabilization Of Lithosol Yellow.

A series of cream enamels were prepared with a pigment ratio of 95 parts Titanium Dioxide and 5 parts Lithosol Yellow at approximately 6% total pigment content. One of these contained 0.3% citric acid to serve as a standard. The remaining enamels were acid-free and in these a small portion of the TiO_2 was replaced stepwise, introducing zinc oxide in the amounts of 0.20%, 0.35% and 0.65%. (Approximately 2, 5, and 10 percent respectively of the total pigment content).

Graph I shows the color change which resulted on accelerated aging of these enamels in the wet state. (See Appendix for a description of the accelerated aging test and method of color drift evaluation with Hunter Multipurpose Reflectometer).

In the initial experiments the accelerated aging test had not been refined; consequently, in order to describe this first series of tests on a basis comparable to the graphs which follow, the period between one and five days on the curves of Graph I has been estimated in the light of what was learned in later experiments; namely, that maximum color change takes place between 1 and 3 days.

Curve 1 reveals the large color change which resulted in a cream formulation containing 0.3% citric acid. This acid content is normally found in 253 and 246 line tinting enamels and

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finished products. In curve 2 the performance of an acid-free unstabilized cream formulation is described. It will be be realized here that the removal of citric acid (G-499) from the formulation greatly reduced the color change, but the color drift caused by the acidity of the nitrocellulose vehicle was still objectionable. Curves 3, 4 and 5 show the reduction in color change with the introduction of increasing amounts of zinc oxide (0.25%, 0.35% and 0.65% respectively).

The cause for the return to a lighter shade than at the beginning of the test in curves 4 and 5 is attributed to the use of an unstablized Lithosol Yellow Tinting enamel which had undergone a slight color change before being let down with the Titanium Dioxide enamel. The change in acidity caused by the introduction of zinc oxide promoted a color change in the opposite direction, revealing the color shift to be reversible. This fact brought out the need for initial stabilization of the Lithosol Yellow Enamel with zinc oxide in the mill base as well as in the final formulation.

Milling Lithosol Yellow pigment with citric acid to induce full color change initially was presumed to be no solution, since the acid content would change in the reduction of the mill base to a tinting enamel and again, when the enamel was blended to produce tints. Experiments conducted by the Newark Pigments Department on this factor bear out this conclusion. Creams prepared in this manner had a tendency to become lighter in the wet state.

<u>The Effect Of Zinc Oxide On The Color Stability of Lithosol Yellow In The Presence of Citric Acid.</u>

Since many of the cream formulations use several 253 line tinting enamels to produce to the desired color, additional experiments were conducted with creams prepared from a zinc oxide stabilized Lithosol Yellow Tinting enamel which contained 0.5% ZnO. This enamel was let down with an acid free titanium dioxide tinting enamel to a formulation having a pigment ratio of 95 parts white to 5 parts of Lithosol Yellow. By partial replacement of the TiO_2, the zinc oxide content was again varied up to 0.5% of the total formulation in the presence of 0.3% citric acid.

From previous experience in white formulations the indescriminate use of zinc oxide in films was known to induce objectional chalking in the lighter colored "Duco" enamels; however, small amounts had been used in maroon and blue formulations without difficulty. Based on this experience the safe limit of zinc oxide was set at 0.5% maximum or roughly 5% of the normal pigment content.

In Graph II the curves represent the effect on color stability of increased amounts of zinc oxide up to 0.5% with the standard amount of citric acid present (0.3%). From these curves, it becomes quite clear that the maximum permissible amount of zinc oxide could in no way compensate for this quantity of citric acid. The optimum zinc oxide concentration appeared

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to be in the neighborhood of 0.35%; a further increase in zinc oxide above this amount does not result in a proportionate reduction in color change.

In Graph III, the zinc oxide content was maintained at 0.5% zinc oxide and the citric acid content was varied from zero up to 0.2%. These increments represent the amount of acid introduced into a formulation when a 253 or 246 line acid-containing tinting enamel comprises 5%, 10%, 20%, 30%, 50% and 66% of the formulation. The dotted lines here, enclose the area of acceptable color stability at 0.5% zinc oxide as observed visually. It can be seen that at such a concentration of zinc oxide the quantity of acid-containing tinting enamels can comprise up to 20% of the formulation.

Preparation of Actual 1949 Creams On The Lithosol Yellow Basis.

Since in normal cream formulations acid containing tinting enamels would rarely exceed 5% of the total formulation for delicate tinting purposes, it was decided to further limit the zinc oxide content to 0.35% to insure freedom from excessive chalking. Both Nankeen Cream (253-5265) and Sequoia Cream (253-52881) were prepared in such a manner and tested for color stability on accelerated aging in the wet state. Reference to Graph IV reveals the adequate wet state color stability of these enamels.

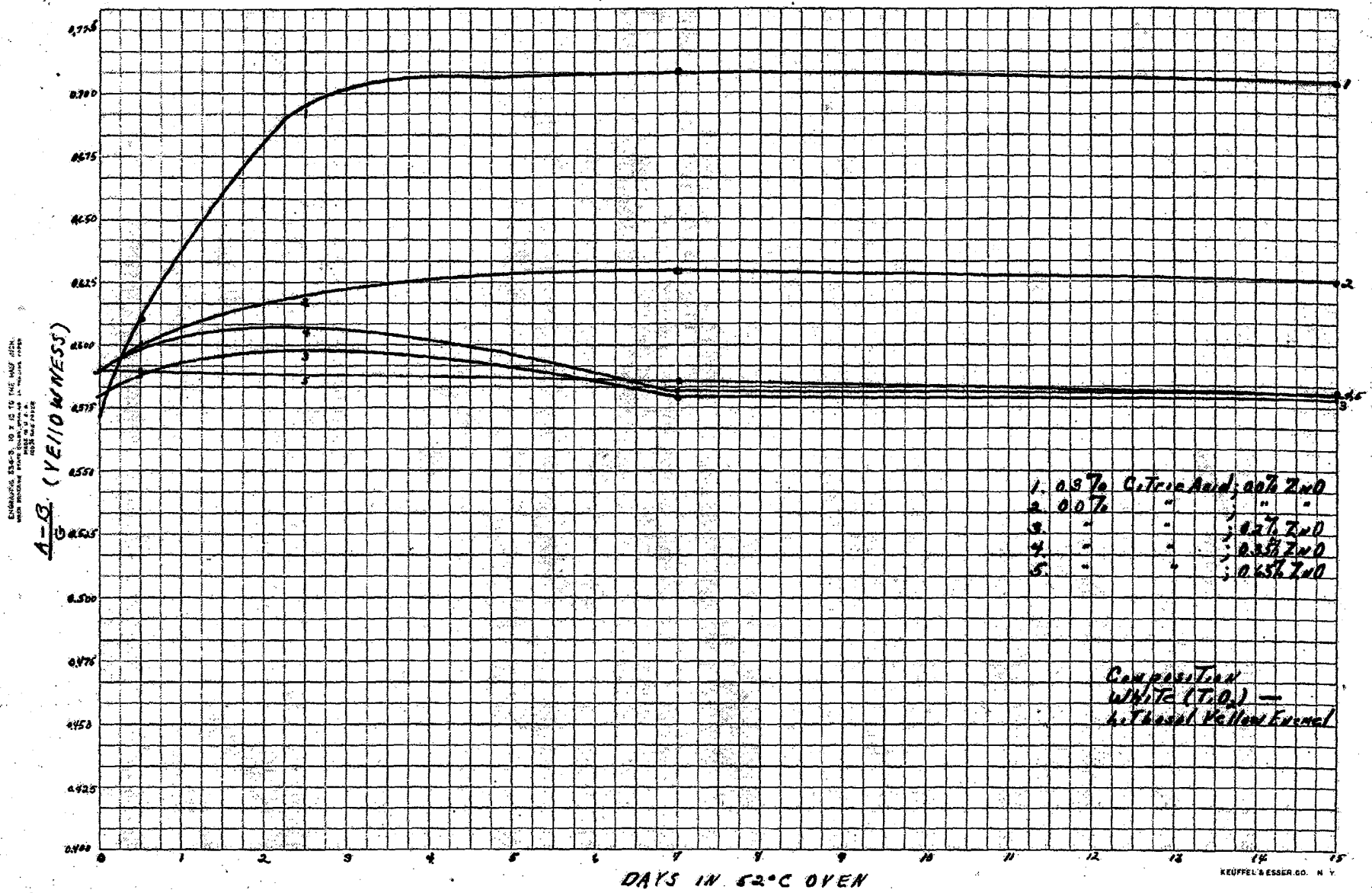
In addition to the above tests, adhesion and flexibility, water soak, hiding power and buffing were compared with standard formulations and in all cases those based on Lithosol Yellow were equal to or superior to standard. Six month's exposure panels have established the superior light fastness of creams based on Lithosol Yellow and no excessive chalking has resulted to date.

Bright Yellow "Ti-Tint"

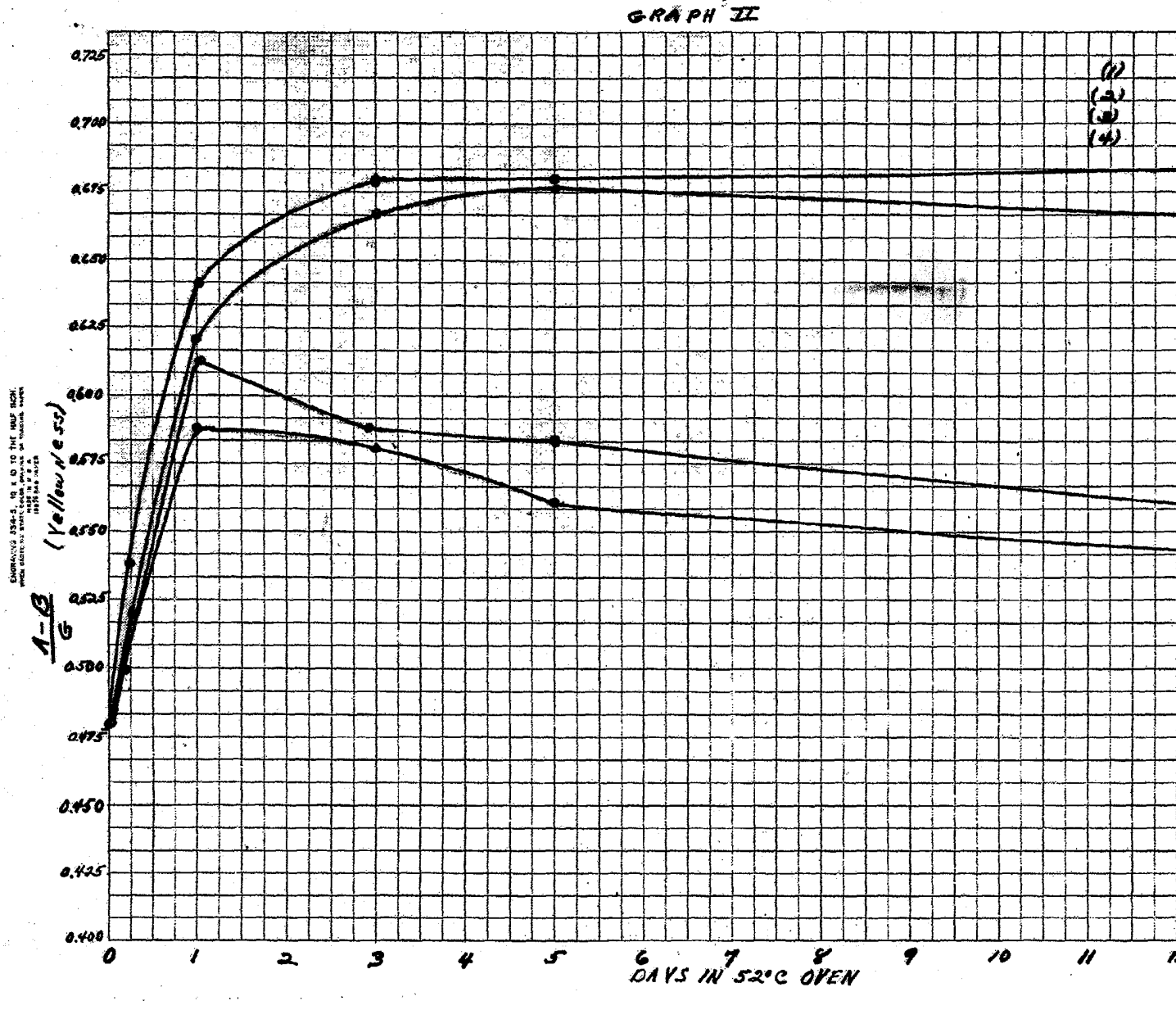
This pigment was formulated into a tinting enamel and tested for wet state color stability in a similar manner to Lithosol Yellow. It has adequate wet state color stability in the presence of citric acid and re-exposure of the pigment in a cream formulation confirmed its excellent light fastness. However, due to its weak tinting strength all creams were not possible through its use without resorting to chrome yellow. Consequently, no additional work was done on it and all energy was directed toward the stabilization of Lithosol Yellow.

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GRAPH I

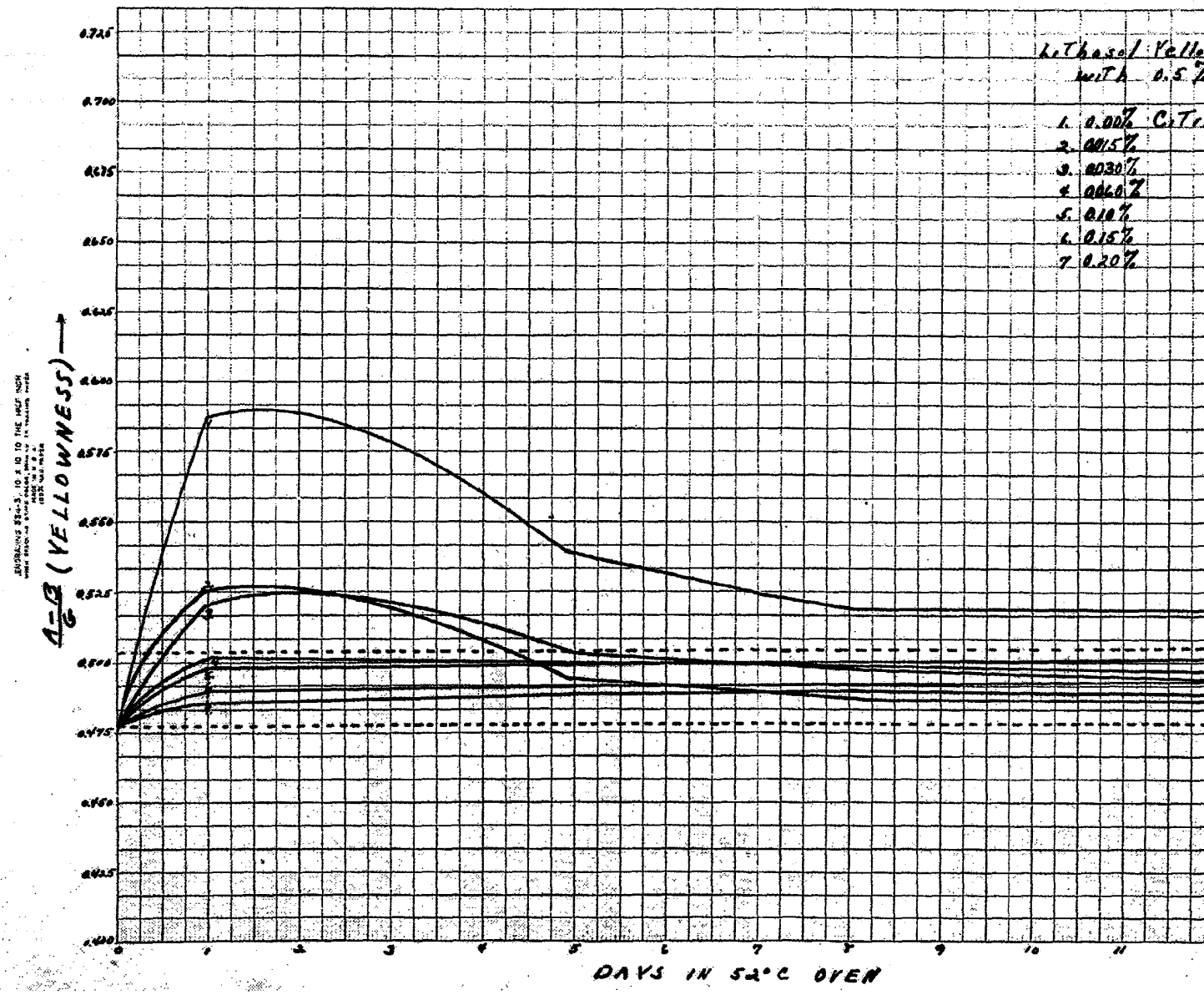


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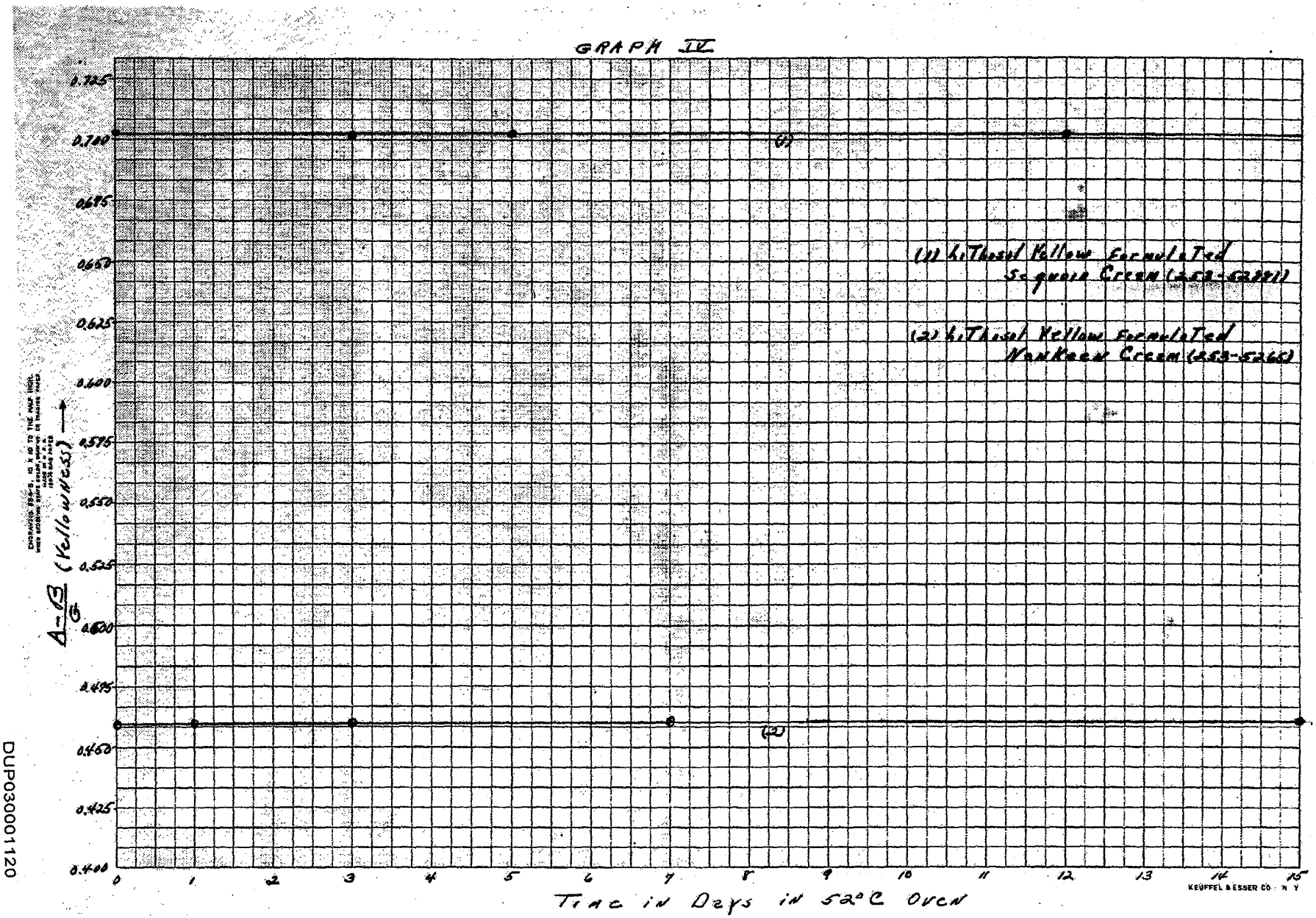


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GRAPH III



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APPENDIX

Accelerated Aging Test at 52°C.

In all the experimental work on checking the wet-state color of the cream formulation 300 g samples were prepared and placed in 16 oz. glass jars. Before placing these samples in the 52°C. oven, a portion was removed and an original color card standard prepared. Thereafter, these test samples were removed from the oven at the intervals indicated in the curves. Samples were cooled, thoroughly mixed, a portion removed, a color card sprayed, and the remainder of the sample returned to the oven to continue aging.

Color Change Evaluation

The color change which occurred on accelerated aging was evaluated both visually and with the aid of the Hunter Multipurpose Reflectometer (1). Since this change on aging was in all cases to a more intense yellow color and return, a procedure for measuring yellowness was used. The procedure consisted of obtaining the tri-color stimulus reflectance readings with the Hunter instrument after calibration with suitable secondary standards with reflectances values in the region of the samples under test. A calculation was made of the following quantity:

$$\frac{A - B}{G} = \text{Yellowness}$$

when A = value of reflectance with the Amber filter
B = " " " " " Blue "
G = " " " " " Green "

It was found that this quantity when plotted against time, described in a quantitative fashion the color change of the test color cards as observed qualitatively with the eye.

(1) Photoelectric Tristimulus Colorimetry with Three Filters, National Bureau of Standards Circular No. 429 (1942).

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