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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

EVALUATION OF ZIRCONIUM OXYCHLORIDE AS
PRECIPITANT FOR ACID DYES.

Period Covered: April 9, 1946 to April 29, 1946

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Final Report

Title: Evaluation of Zirconium Oxychloride as Precipitant for Acid Dyes.

Period Covered: April 9, 1946 to April 29, 1946.

SUBMITTED BY: F. K. Schaefer

DATE SUBMITTED: 6/27/46

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I. INTRODUCTION

The Titanium Alloy Mfg. Co. in their bulletin entitled The Role of Zirconium Salts in the Preparation of Unusual Pigments advocated the use of zirconium oxychloride as precipitant for various dyes. Considering this report it was decided that we try to prepare zirconium pigments of some of our more common dyes, e.g. Peacock Blue, Scarlet 2R, Orange II and "Lithosol" Red 2B.

II. SUMMARY AND CONCLUSIONS

Zirconium toners of Orange II, Scarlet 2R, "Lithosol" Brilliant Blue E and "Lithosol" Red 2B dyes and lakes of Orange II, Alizarine, Scarlet 2R, "Lithosol" Brilliant Blue E, dyes were prepared. Procedures given in Tamco's bulletin were followed and other than those our regular standard formulas were used. In the latter zirconium oxychloride was substituted for barium or calcium salts on the basis of tabulated ratios given in Tamco's bulletin.

Considering the cost of zirconium oxychloride (35¢ per lb.) versus the cost of barium chloride (4¢ per lb.) and the cost of calcium chloride (3¢ per lb.), the zirconium pigments would have to have exceptional qualities to warrant the additional expense.

The following points will summarize results:

- 1) The zirconium toner of Orange II was blue and strong versus the barium toner (K-2273) and consequently, seemed to be of interest. However, the substitution of zirconium in the Persian Orange Lake (YL-61-D) resulted in a blue and weak lake versus control. A mechanical mix of the Zr toner and hydrate base to equal the lake showed that the toner had strength only equal to the lake of YL-61-D type.
- 2) The substitution of zirconium for aluminum and barium in the BL-72-D procedure resulted in a very weak and very dull product. The zirconium toner of "Lithosol" Brilliant Blue E (dye used in BL-72-D) was poor in strength. Lightfastness was not improved by zirconium.
- 3) The zirconium toner of Scarlet 2R was dull and weak versus the barium toner and the lake of the former was blue and weak versus the lake of the latter.
- 4) In the RT-332-D procedure (Alizarine lake) the substitution of zirconium for calcium resulted in a very weak and very dull product.
- 5) In the K-1630 process (RT-428-D type - "Lithosol" Red 2B/ "Lithosol" Red 2B D eyes), the substitution of zirconium for calcium resulted in a product with dark and intense maroons and weak tint. This product is being tested as a paint pigment versus RT-428-D and RT-525-D.

6) The filtration of alumina hydrate lakes struck with zirconium was almost impossible due to the highly deflocculated nature of the suspension.

To summarize, the use of zirconium oxychloride as a precipitant for acid dyes does not appear to possess any merit on the basis of the results obtained.

III. GENERAL DISCUSSION

A. Zirconium toner and lake of Orange II dye.

The zirconium toner of Orange II was prepared according to the procedure from the bulletin: The Role of Zirconium Salts in the Preparation of Unusual Pigments - Titanium Alloy Mfg. Co., 2/15/44. No difficulty was encountered in the preparation of this pigment. It was tested against K-2273 (barium toner of Orange II) by rub-out in varnish drier and found to be very dark in manganese, blue and very strong in undertone, and blue and strong in tint. The product was worse than K-2273 in lightfastness after twenty-four hours fadeometer exposure. In alcohol bleed the product was very poor - slightly worse than K-2273.

The XE-61-D procedure (Persian Orange Lake) was followed in preparing the zirconium lake of Orange II. Zirconium oxychloride was substituted for the barium chloride on an equivalent basis but about 30% additional zirconium oxychloride was required to eliminate bleed. This pigment was almost impossible to filter, because a colloidal suspension seemed to be set up. Consequently, washing was eliminated. Compared to Persian Orange Lake, the zirconium lake of Orange II was slightly dark in manganese, slightly blue in undertone, and blue and slightly weak in tint. It was slightly worse than the control in lightfastness and equal to it in alcohol bleed - poor.

B. Zirconium toner and lake of Scarlet 2R

This toner was prepared exactly as the toner of Orange II but an excess of about 20% zirconium oxychloride was required to eliminate bleed. Versus the barium toner of Scarlet 2R, the zirconium toner was light in manganese, blue in undertone, and blue and weak in extension. Both products were alike in lightfastness but the zirconium pigment was better in alcohol bleed.

The same difficulties that were encountered in preparing the zirconium lake of Orange II were encountered in preparing the zirconium lake of Scarlet 2R. About a 20% excess in zirconium oxychloride was required to eliminate bleed. In this case barium chloride was added to precipitate sulfates, etc. The zirconium lake was dark in manganese, very weak in both undertone and tint versus BE-35-D, the barium lake. The two were equal in lightfastness and in alcohol bleed.

C. Zirconium pigment of Alizarin Red Paste

The BE-352-D procedure (hydrate lake of alizarine struck with calcium) was followed and zirconium oxychloride substituted for calcium chloride on equivalent basis. No bleed showed up by spot test. Although filtration of the lake was not rapid, it was an improvement over the two above mentioned zirconium lakes. The resulting pigment was dark in manganese, very dull and

weak in undertone, and very weak in tint versus the control. It was worse than control in both lightfastness and in alcohol bleed.

D. Zirconium pigment of "Lithosol" Brilliant Blue E

At first a zirconium pigment of "Lithosol" Brilliant Blue E was made following the BL-72-D procedure. Zirconium oxychloride was substituted for both the aluminum and barium chlorides. The usual difficulties were encountered:

- 1) A 30% increase in zirconium oxychloride was required to eliminate bleed.
- 2) A colloidal suspension formed which was almost impossible to filter.

The resulting zirconium lake was equal in masstone, weak in undertone, and very weak in tint versus the aluminum/barium control. Both were equal in lightfastness being very poor. The zirconium pigment was worse in alcohol bleed.

Since the above attempt to form a good pigment failed, an attempt to prepare the zirconium pigment of "Lithosol" Brilliant Blue E using the Acid Green formulation written up in Tazoo's report (See A of General Discussion) was made. A barium control was attempted but no pigment formed. The zirconium pigment formed but even upon the addition of 60% zirconium oxychloride in excess, bleed was not eliminated. The product was extremely weak as noted by a mix made of it comparable to BL-72-D. It was also very, very poor in lightfastness and very poor in alcohol bleed.

E. Zirconium pigment of "Lithosol" Red 2B/"Lithosol" Red 2BD

The K-1030 (RT-428-D type) procedure was followed in the preparation of this pigment. The calcium chloride was substituted by zirconium oxychloride on equivalent basis. No difficulties were encountered in the preparation of the pigment. The resulting product was very dark in masstone, yellow and weak in undertone and weak in tint versus control. It was also worse than control in lightfastness and in alcohol bleed. However, due to the depth of masstone this pigment is being tested as a paint pigment.

IV. EXPERIMENTAL METHOD

<u>Notebook No.</u>	<u>Description</u>
1017-33	Zirconium toner of Orange II
-34	" " and lake of Scarlet 2B.
-35	" lake of "Lith." Brilliant Blue E.
-36	" " of Alizarin.
-37	" " of Orange II.
-39	" " of Scarlet 2B.
-40	" " of "Lith." Red 2B/ "Lith." Red 2BD.
-45	" toner of "Lith." Brilliant Blue E.

V. REFERENCES

- A) The Role of Zirconium Salts in the Preparation of Unusual Pigments - Titanium Alloy Mfg. Co.
- B) Letter of A. Siegel to A. A. Brinckman on Zirconium Pigments, 3/12/46.