Copy No. KM-44-24
/

E. I. DU PONT DE NEMOURS & COMPANY
KREBS PIGMENTS DEPARTMENT
256 VANDERPOOL STREET
NEWARK, NEW JERSEY



# NEWARK PLANT
# PIGMENT COLOR RESEARCH REPORT

Final Report

An Investigation of the Determination of Total Alkali Metals in Zinc Yellow.

Period Covered: Jan. 5, 1944 to March 20, 1944

FILE: 212

DATE: 4/25/44

Serial No. KN-44-24

Copy No. /

Copy to:

#1 - Numerical File ✓
2 - Research Office (212)
3 - Library File (212)
4 - Imperial Chemical Industries, Ltd.
5 - " " " "
6 - " " " "
7 - Mr. C. H. Rupprecht, Wilmington (ICI File)
8 - Dr. J. W. Stillman, Exptl.Station, Wilm.
9 - " " " " " "

NEWARK PLANT

# PIGMENT COLOR RESEARCH REPORT

## Final Report

**Title:** An Investigation of the Determination of Total Alkali Metals in Zinc Yellow.

**Period Covered:** Jan. 5, 1944 to March 20, 1944

SUBMITTED BY: A.R. Hanke & S.W. Rumbel DATE SUBMITTED: 3-30-44

APPROVED BY: A.A. Brizzolara 4/25/44 DATE ISSUED: 4/25/44

INTRODUCTION:

The present method, KCR #46, for determining total alkali metals involves the precipitation of the chromate with lead acetate, followed by the precipitation of the excess lead and the zinc with $H_2S$. The alkali metals in the filtrate are converted to the sulfate and weighed as such. A copy of that part of KCR #46 which deals with the determination of total alkali metals is attached to this report. See Appendix I.

It was observed that when KCR #46 was followed explicitly, the alkali metal residue almost invariably contained varying small amounts of lead, zinc, iron, and occasionally chromium. It was also observed that a sample supposedly free of alkali metals gave results varying from 2.03% $K_2O$ to 0.99% $K_2O$, and that in general the variation in the analysis of normal zinc yellow was rather large. The purpose of this work was to investigate the causes of this variation and to improve the method for determining alkali metals.

SUMMARY AND CONCLUSIONS:

1) Wide variations have been observed when using KCR #46 to determine alkali metals in zinc yellow.

2) Positive errors are introduced because the alkali metal residue contains varying amounts of heavy metals.

3) Negative errors are introduced because there is some loss of alkali metals due to adsorption and operative technique. This negative error is a function of the sample weight and also a function of the amount of alkali metal in the sample. For a 2 gram sample, of a normal zinc yellow, the negative error is about 14% relative and drops to about 1.5% for a 1 gram sample. For samples less than 1 g, the negative error again seems to increase slightly.

4) There is no simple way to correct for the negative error. If the sample contains a normal amount of alkali metals, 1.5% of the amount found can be added but since the proper amount to add will vary somewhat depending on the individual technique of the operator, type of filtering equipment, etc., the proper amount to add should be determined by running controls. Another objection to this method of correction is that the percentage adsorption is not a linear function of the amount of alkali metal present although for small variations in percent alkali metal such can be assumed.

5) The positive error can be reduced to a minimum by following the procedure outlined in detail in another section of this report. See Appendix II.

EXPERIMENTAL:

Table 1 shows typical results when determining alkali metals following KCR #46.

Table 1.

Typical Results when following KCR #46 for Total alkali metals

| No. | Source of Data | Total Alkali Metals as $\%K_2O$ | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 1 gram sample | | | 2 gram sample | | 5 g sample | |
| 1 | NB-1050-51 | 10.25 | | | | | 9.26 | 8.62 |
| 2 | " | 10.35 | | | | | 9.01 | 8.96 |
| 3 | NB-1050-55 | 11.25 | 11.24 | | | | | |
| 4 | " | 8.03 | 8.68 | | | | | |
| *5 | " | 2.03 | 1.37 | 0.99 | | | | |
| 6 | " | 13.03 | 13.35 | | | | | |
| 7 | NB-1000-54 | | | | 6.95 | 6.87 | | |
| 8 | " | | | | 3.82 | 3.99 | | |

* This sample actually contains only traces of alkali metals.

From the above table, it can be seen that although there are some good checks, the variation as a whole is too great, the results are dependent on the sample weight, and judging from the results of sample C, the results are high when the amount of alkali metals present is small. Experiments that will be described later will substantiate these conclusions.

A qualitative analysis of the alkali metal residue showed the presence of small amounts of lead, zinc, and iron. No quantitative results were obtained on the heavy metals present but it was obvious that the amount remaining varied widely from determination to determination.

The buffer system used in KCR #46 is acetic acid, acetate and it was observed that during the course of the precipitation of the sulfides, the pH changed from pH 3.6 to pH 3.1. Zinc sulfide will precipitate quantitatively over this pH range but the best pH range is between pH2 and pH3. If the pH gets much above pH3, the zinc sulfide precipitate is difficult to filter. A popular buffer system for precipitating zinc sulfide is formic acid, formate. This was tried but was discarded when it was observed that the formic acid reduced some of the chromate and that the final alkali metal residue contained some trivalent chromium.

Since it appeared that the heavy metals found their way into the alkali metal residue because of failure to precipitate completely in a filterable form, attention was centered on more efficient precipitation of the sulfide in the acetic acid - acetate buffer system. Kolthoff & Moltsan(1) have shown that small amounts of mercury have a pronounced effect on the post precipitation of zinc sulfide. The addition of a small amount of mercury was tried as a means of more efficiently removing the zinc as the sulfide. This was not effective and small amounts of mercury were detected in the alkali metal residue.

Other ideas suggested themselves. The solution was boiled to a small volume after the initial separation of the sulfides and the solution was resaturated with $H_2S$. This almost invariably brought down more zinc sulfide but the alkali metal residue still contained some zinc. Gentle ignition of the residue, leaching with water, filtering and re-evaporation of the filtrate helped to clean up the alkali metal residue but some zinc still remained. When the leached alkali metal residue was treated with a few drops of ammonium hydroxide, some improvement in cleaning up the alkali metal residue was noted. A small amount of ammonium carbonate in connection with the ammonium hydroxide also helped, but still some zinc remained in the alkali metal residue. The best single treatment found for cleaning up the alkali metal residue, was to leach the gently ignited alkali metal sulfates with water, saturate with $H_2S$ and filter. The evaporation of the clear filtrate yielded alkali metal sulfates that contained only a trace of zinc.

A series of experiments were performed in which solutions of potassium chloride, sodium chloride, chromic acid, and zinc oxide were mixed and the alkali metals determined. Reagent grade chemicals were used and the alkali metal solutions were accurately prepared and measured for use so that the amount of alkali metal present for each determination was always known. The solutions were prepared as follows:-

1) Zinc - 8 g ZnO dissolved in a mixture of 50 ml water and 12 ml acetic acid. Then making to 100 ml with distilled water (5 ml 0.4g ZnO).

2) Chromic Acid - 8 g $CrO_3$ made up to 100 ml with distilled water. (5 ml 0.4 g $CrO_3$).

3) Sodium Chloride - 3.772 g NaCl made accurately to a volume of 100 ml with distilled water. (5 ml 0.1 g $Na_2O$).

4) Potassium Chloride - 3.166 g KCl made accurately to a volume of 100 ml with distilled water. (5 ml 0.1 g $K_2O$).

Amounts of these solutions were taken to simulate a zinc yellow of composition 40% $CrO_3$, 40% ZnO, and 10% $K_2O$. This was considered close enough to the actual composition of a zinc yellow for the purpose intended. The methods used were basically that of KCR #46 with modifications which will be enumerated below.

1) Double sulfide precipitation - This follows the regular method through the precipitation of the sulfides. After filtration, the solution is evaporated to a volume of about 100 ml and then re-saturated with $H_2S$. The rest of the procedure is the same as the regular method.

2) Alkali metal leach - This modification takes the final alkali metal residue, leaches it with hot water, and then filters. The filtrate is evaporated to dryness and gently ignited.

3) Alkali metal leach + $H_2S$ - This is the same as 2 but after leaching, the solution is saturated with $H_2S$ before filtering.

4) Alkali metal leach + $NH_4OH$ - This is the same as 2 but a few drops of $NH_4OH$ are added before filtering.

5) 8-hydroxyquinoline method - This takes the chromate out as lead chromate similar to the regular method but the excess lead and the zinc are taken out with 8-hydroxyquinoline, (30 ml of 5% alcoholic solution). This latter precipitation was carried out in two modifications, namely, in slight acetic acid solution and in slight ammonium hydroxide solution.

These above modifications were at times used in combination; that is, results on the double sulfide method were obtained with and without an alkali metal leach. Table 2 consolidates the data.

## TABLE 2.

### TOTAL ALKALI METAL DETERMINATIONS ON KNOWN MIXTURES OF ZINC, CHROMIUM, POTASSIUM & SODIUM

Notes: 1) The theoretical amount of $K_2O$ for each of the series is equal to the grams of $K_2O$ equivalent as indicated in the composition column. This can be compared directly with the figures in the last column.

2) Where there are two methods indicated for a single series, each vertical column of two figures represents data from the same sample, i.e., in series 3, the vertical figures 0.173 g and 0.167 g may be directly compared because both figures are derived from the identical sample.

| Series | Composition of Sample expressed as oxides | Equivalent sample wt. of zinc yellow | Method | Weight of alkali metal residue found expressed as grams $K_2O$ | | | |
|---|---|---|---|---|---|---|---|
| 1 | 0.8g ZnO+0.8g $CrO_3$ + 0g $K_2O$ | 2 grams | Regular KCR #46 | 0.0010g | 0.0014g | | |
| 2 | 0.8g ZnO + 0.8g $CrO_3$ + 0.2g $K_2O$ | 2 grams | Double sulfide pptation. | 0.178g | 0.187g | | |
| 3 | " " " " | 2 grams | Double sulfide pptation. | 0.173g | 0.175g | | |
| | | | " " " + alk.metal leach | 0.167g | 0.164g | | |
| 4 | 0.8g ZnO+0.8g $CrO_3$ + 0.1g $Na_2O$+0.1g $K_2O$ (Theoretical $K_2O$=0.224g $K_2O$ | 2 grams | Double sulfide pptation. | 0.182g | 0.182g | | |
| | | | " " " + alk.metal leach | 0.179g | 0.183g | | |
| 5 | 0.8g ZnO+0.8g $CrO_3$ + 0.2g $K_2O$ | 2 grams | Regular KCR #46 | 0.168g | 0.185g | 0.183g | 0.176g |
| | | | " " " + alk.metal leach | 0.167g | 0.183g | 0.174g | 0.174g |
| 6 | 0.8g ZnO+0.8g $CrO_3$ + 0.2g $K_2O$ | 2 grams | Double sulfide pptation. | 0.168g | 0.185g | 0.179g | 0.178g |
| | | | " " " + alk.metal leach | 0.157g | 0.177g | 0.169g | 0.171g |
| 7 | 0.2g $K_2O$ | 2 grams | Double sulfide pptation. | 0.198g | 0.196g | | |
| 8 | KCl equiv.to 0.2g $K_2O$ | 2 grams | Oven dried at 110°C | 0.204g | 0.201g | | |
| 9 | " " " " " | 2 grams | Treat with acetic acid & $H_2SO_4$. Evap. to dryness and weigh as sulfates | 0.201g | 0.203g | 0.204g | |
| 10 | 0.4g ZnO+0.4g $CrO_3$ + 0.1g $K_2O$ | 1 gram | Regular KCR #46 | 0.103g | 0.103g | 0.109g | 0.104g |
| | | | " " " + alk.metal leach + $H_2S$ | 0.0979g | 0.0973g | 0.1003g | — |

| Series | Composition of Sample expressed as oxides | Equivalent sample wt. of zinc yellow | Method | Weight of alkali metal residue found expressed as grams $K_2O$ | | | |
|---|---|---|---|---|---|---|---|
| 11 | 0.4g ZnO+0.4g $CrO_3$ + 0.1g $K_2O$ | 1 gram | Double sulfide pptation. | 0.1103g | 0.1107g | 0.1077g | 0.1028g |
| | | | " " " + alk.metal leach +$NH_4OH$ | 0.1066g | 0.1088g | 0.1069g | 0.1006g |
| 12 | 0.3g ZnO+0.3g $CrO_3$ + 0.06g $K_2O$ | 0.6 gram | Regular KCR #46 | 0.1235g | 0.1216g | 0.1308g | 0.0741g |
| | | | " " " + alk.metal leach+$H_2S$ | 0.0541g | 0.0541g | 0.0543g | 0.0497g |
| 13 | 0.3g ZnO + 0.3 $CrO_3$ + 0.06g $K_2O$ | 0.6 gram | Regular KCR #46 | 0.0591g | 0.0601g | 0.0613g | |
| | | | " " " + alk.metal leach + $H_2S$ | 0.0579g | 0.0573g | 0.0595g | |
| 14 | " " " " " | 0.6 gram | 8-hydroxyquinoline in gl acetic acid solution. | 0.0607g | 0.2675g | 0.2429g | 0.2597g |
| | | | Same as above but in addition leach + $H_2S$ | 0.0566g | 0.0577g | 0.0562g | 0.0564g |
| 15 | " " " " " | 0.6 gram | 8-hydroxyquinoline in sl.$NH_4OH$ solution | 0.0628g | 0.0648g | | |
| | | | " " " " " + alk.metal leach | 0.0573g | 0.0552g | | |
| 16 | " " " " " | 0.6 gram | 8-hydroxyquinoline in sl.$NH_4OH$ solution | 0.0696g | | | |
| | | | " " " " +leach + $H_2S$ | 0.0556g | | | |

From the data of Table 2 the following observations can be made:-

1) For normal zinc yellows, using a 2 gram sample, and KCR #46, the negative error is greater than the positive error, i.e., the results are low. (See series 2,3,4 & 5).

2) For a 1 gram sample, the reverse is true. The overall error is about 6.4% high with a large variation (compare series 10 & 11 with theoretical).

3) A double sulfide precipitation offers no advantage over the regular KCR #46 (compare series 2,3,5,& 6; also 10 & 11).

4) An alkali metal leach + $H_2S$ is more effective in purifying the alkali metal residue than an alkali metal leach + $NH_4OH$. (Compare series 10 & 11).

5) The blank amounts to about 0.0011 g $H_2O$ for a 2 g sample and the standard potassium chloride solution gives the theoretical result in the absence of other ions with an accuracy of about 2% relative. (See series 1, 7, 8, 9)

6) If we assume that an alkali metal leach will remove all heavy metals from the alkali metal residue (not strictly true), the negative error for a 2 gram sample will be the average of the alkali metal leach determinations of series 3, 4, 5, 6, subtracted from their theoretical values. This amounts to -0.0297g or 14.8% relative. Actually the alkali metal residue still contains some alkali metals so 14.8% is a minimum figure, the true figure being even higher.

7) If we assume that an alkali metal leach + $H_2S$ will remove all heavy metals, and this by qualitative analysis does get very nearly all of the heavy metals, the negative error for a 1 gram sample may be obtained from series 10. This amounts to - 1.5% relative. This is the best figure that has been obtained.

8) For a 0.6 g sample, the negative error is about 3% relative. This figure was obtained from series 13. Series 12 was not used because the results are abnormal and serve to indicate how KCR #46 can at times fail and give results that are far too high.

9) 8-Hydroxyquinoline in acetic acid solution does not work (see series 14).

10) 8-Hydroxyquinoline in $NH_4OH$ solution works better but not as efficiently as $H_2S$ in removing heavy metals (compare series 13 & 15).

11) The negative error may be slightly higher when using

8-hydroxyquinoline (see series 16).

## SUGGESTIONS FOR FURTHER RESEARCH

1) The use of a small amount of gelatin to coagulate the sulfides should be further investigated. Caldwell & Moyer (2) have used gelatin to flocculate sulfide precipitates. Preliminary observations indicate that this will prove useful not only in getting more complete separation of the heavy metals but also in decreasing the negative error. The use of gelatin is incorporated in the modified procedure.

2) Try to employ 8-hydroxyquinoline or some other precipitating agent wherever $H_2S$ is used, eliminating the need for $H_2S$. Preliminary investigations indicate that $H_2S$ is superior to 8-hydroxyquinoline but with modifications or where speed is required at the expense of accuracy, some organic precipitant may prove useful.

3) Consider the determination of potassium and sodium separately and in the presence of the zinc and chromium. Potassium as the perchlorate and sodium as the zinc or magnesium uranyl acetate salt should be considered. Concerning the uranyl acetate reagents for sodium a large bibliography with comments has been compiled by T.T. Collins, Jr. (3).

4) The use of a radioactive method depending on the radioactivity of a potassium isotope may prove useful for determining potassium in special cases. (4).

## REFERENCES

(1) Kolthoff & Moltsau. J.Phys. Chem. 40, 779 (1936)

(2) Caldwell & Moyer. J.A.C.S. 57, 2372 (1935)

(3) Theron T. Collins, Jr. "Determination of Sodium with Uranyl Acetate Reagent". Document #1798. American Document Institute, Washington, D.C.

(4) Barnes & Salby. Ind. Eng. Chem. Anal Ed. 15, 4 (1943)

The experimental record is to be found in:-

N.B. 1050-64
N.B. 1050-66

## APPENDIX I

### TOTAL ALKALI METALS IN ZINC YELLOW
(Abstracted from KCR #46)

Dissolve 1 gm. of Zinc Yellow in 10 cc. of (1:1) acetic acid, add 25 cc. $H_2O$ and heat until in solution. Dilute to approximately 250 cc. and heat to boiling. Add 20 cc. of 10% $Pb(Ac)_2$ and allow to settle. Filter and wash well with hot $H_2O$. Saturate the filtrate with $H_2S$, passing $H_2S$ through the solution at a rapid rate (at least 8 bubbles/sec.) for at least 40 min., keeping the temperature below 50°C. Zn and excess lead will be precipitated. Filter and wash with cold $H_2O$. (It is necessary to keep down the concentration of $HAc$ to ensure complete removal of the Zn). Boil to expel $H_2S$. Add 3 cc. $H_2SO_4$ and boil down to a small volume. Transfer to a weighed silica dish and evaporate to dryness on a hot plate. Heat to complete dryness on a Bunsen burner. Add solid $(NH_4)_2CO_3$. Heat till volatilized. Repeat 4 times. Cool. Weigh. Add a few crystals of $(NH_4)_2CO_3$, and again heat till volatilized. Cool, weigh, and repeat to constant weight.

$$\frac{\text{wt. alkaline } \overline{SO}_4 \times 100}{\text{wt. of sample}} = \% \text{ total alkaline sulphate } (Na_2SO_4 \text{ and } K_2SO_4)$$

$$\% K_2SO_4 \times .541 = \% K_2O$$

Report as $\% K_2O$

## APPENDIX II

### DETERMINATION OF TOTAL ALKALI METALS IN ZINC YELLOW PIGMENTS

### Modified Procedure

I. Reagents

1) Acetic acid - C.P. (1:1)
2) Lead Acetate C.P. Neutral (10% solution)
3) Hydrogen sulfide
4) Sulfuric acid - C.P. (1:1)
5) Ammonium carbonate - C.P.
6) Gelatin, Low ash - (0.02% solution)

II. Procedure

Dissolve 1.0000 g of zinc yellow in 10 ml of 1:1 acetic acid and add 25 ml water. Heat until dissolved. Dilute to ± 250 ml and heat to boiling. Add 20 ml of 10% lead acetate and allow the precipitate to settle. Filter and wash the precipitate with hot water. Saturate the filtrate with $H_2S$ for about 40 min. Add 10 cc. of a 0.02% solution of gelatin and stir vigorously. Filter and wash with $H_2S$ water slightly acidified with a few drops of 1:1 sulfuric acid. Add 5 ml of 1:1 sulfuric acid to the filtrate and boil to a volume of ± 50 ml. Transfer to a silica dish and evaporate to dryness. Gently ignite until volatile salts are driven off. Leach the residue with hot distilled water, transferring the entire contents to a small beaker. Saturate with $H_2S$ for about 15 min. Add 10 ml of 0.02% gelatin and stir vigorously. Filter and wash as before catching the filtrate in a tared silica dish. Add about 2 cc. of 1:1 $H_2SO_4$ to the filtrate and evaporate to dryness and again gently ignite. During the ignition process add small portions of solid ammonium carbonate. Cool in a desiccator and weigh.

III. Calculations

$$\frac{\text{Weight of alkali metal sulfate}}{\text{Sample weight}} \times 100 = \% \text{ total alkali sulfates}$$

$$\% \text{ total alkali sulfates} \times 0.541 = \% \text{ alkali metals expressed as } K_2O$$