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PIGMENT COLOR RESEARCH REPORT

THE DETERMINATION OF FREE ZINC OXIDE IN ZINC CHROMATE PIGMENTS

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Progress
Final Report

Title: THE DETERMINATION OF FREE ZINC OXIDE IN ZINC CHROMATE PIGMENTS

Period Covered: October 1942 to April 1943

SUBMITTED BY: A. R. Hanks

DATE SUBMITTED: 7/1/46

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THE DETERMINATION OF FREE ZINC OXIDE IN ZINC CHROMATE PIGMENTS

INTRODUCTION

The following report is based on a small amount of work performed off and on with the purpose in mind of showing the presence of free zinc oxide in zinc yellow or related pigments. The presence of zinc oxide in zinc yellow can be due to the deliberate mixing in of zinc oxide or to the use of zinc oxide during manufacture and incomplete conversion to the desired pigment. In either case the detection of zinc oxide by chemical means is complicated by the fact that any chemical action on the pigment will so change the pigment that it will be difficult to state whether the chemical evidence for the presence or absence of Zinc Oxide indicates the condition of the pigment before or after the chemical treatment.

Because of this, attention was turned primarily to physical methods. X-ray diffraction and fluorescence under the action of ultraviolet light were the physical methods examined. A chemical method was also investigated not that it could indicate with certainty the presence of free zinc oxide but because it could give an easy measure of the basicity of the pigment. Such a basicity is expressible as free zinc oxide and any increase over the expected basicity of the pigment would point to the possible presence of free zinc oxide.

SUMMARY AND CONCLUSIONS

1. X-ray diffraction can detect with certainty 1% or more of free zinc oxide in zinc yellow.

2. Fluorescence induced by filtered ultraviolet light was used to detect as little as 0.2% zinc oxide dry ground into zinc yellow. However, two competative samples which contained around 1 to 1 1/2% ZnO by X-ray diffraction analysis showed no fluorescence. This can be considered as some evidence that the zinc oxide present in Reichhold's Zinc Yellow #1420 (C-46530) and a zinc yellow of unknown manufacture C-45839 was not introduced by dry mixing.

3. It is possible to dissolve a zinc chromate pigment in an excess of standard sulfuric acid and back titrate with standard sodium hydroxide solution. There are two points of inflection in the pH curve, one at a pH of 4.0 and the other at about a pH of 8.2. Using the point of inflection at the low pH and knowing the chromate content, it becomes possible to calculate the basicity of the pigment and express it as ZnO. If this turns out to be much higher than expected, free zinc oxide may be present. If the basicity is about that expected, it is very unlikely that any zinc oxide is present.

4. Using these three methods in conjunction with each other can throw some light on the nature of the zinc yellow pigment and how the free zinc oxide, if any, was introduced into the pigment.

5. The most reliable method for detecting ZnO in zinc yellow is by means of X-ray diffraction. Table I shows the results on the samples examined by X-ray diffraction.

TABLE I

ZINC OXIDE IN ZINC YELLOW BY X-RAY

Diffraction

Zinc Yellow Samples	Lattice Spacings	*Percent Oxide Content
Reichhold's 1420 (C-46530)	Normal	1.0
Imperial's K-1970 (C-46315)	"	±0.5
Imperial's K-2062 (C-46632)	"	±0.5
Unknown Mfg. from W. P. Fuller (C-45839)	Slightly shorter	1.5
K-1811 - Lot 6149	Normal	Probably absent
" " 96345	"	±0.5
" " 6068	"	Probably absent

*Anything less than 1% ZnO is in the doubtful range.

EXPERIMENTAL

A. X-Ray Diffraction Method

Samples were prepared by double mix grinding in a micropulverizer mixtures of zinc yellow and zinc oxide. The zinc yellow was K-232-D Lot 93266 and the zinc oxide was Horse Head XX zinc oxide 50 from New Jersey Zinc Co. (D-4273). The samples were made to contain 0, 0.5 1.0, 2.0 and 4.0% ZnO. X-ray diffraction patterns using copper radiation were obtained of these samples along with a sample of the Zinc Oxide. One percent and above could be detected with certainty. One half percent was in the doubtful range. The results when applied to unknown samples of zinc yellow are given in Table I.

B. Fluorescent Method

For this study, the same samples were used as described in section "A". In addition, samples were prepared containing 0.3, 0.2, 0.1, 0.05% Zinc Oxide.

A quartz mercury vapor tube was employed in connection with a suitable Corning light filter to remove the visible light. Small portions of the sample were streaked out on dull black paper and the characteristic fluorescence of the Zinc oxide observed in a suitably darkened room. The sensitivity of the test is admittedly dependant on the intensity of the ultraviolet light, freedom from visible light, etc, but with just ordinary precautions, it was possible to observe a difference between 0 and 0.2% ZnO in zinc yellow.

When this test was applied to the two samples in which ZnO was found by X-ray diffraction, namely C-46530 and C-45839, no fluorescence was observed. The samples were extracted with chloroform to remove any treating agent which it was felt may interfere, but still no fluorescence was observed. The sample was also heated for several days at 165°C. It was thought that the zinc oxide may need to be more nearly dehydrated to properly exhibit fluorescence. Still no fluorescence was observed. Perhaps the zinc oxide is so effectively coated with zinc yellow that the ultraviolet light and fluorescent light are effectively screened. At any rate no further work was done because X-ray diffraction gave results suitable to our purpose. Nevertheless, the fluorescent method was the most sensitive method studied for detecting zinc oxide, the lower limit for the conditions of the experiment being 0.2% ZnO.

C. Basicity Method for detecting Zinc Oxide

This method is admittedly not specific for zinc oxide but if the basicity turns out to be about that expected, the pigment will very likely contain no free zinc oxide.

Since zinc oxide is a basic substance free zinc oxide will increase the basicity of the pigment. If the pigment is dissolved in an excess of a standard acid, the more zinc oxide, the less will be the back titration with standard alkali. A normal zinc yellow pigment very nearly corresponds to the formula,

$$4\ CrO_3,\ 4ZnO,\ K_2O,\ 3H_2O \qquad \text{Mol Wt. } 873.82$$

This may also be written,

$$3\ Zn\ CrO_4.K_2CrO_4.ZnO.3H_2O$$

Thus it is seen that normal zinc yellow already contains the equivalent of one mole of zinc oxide.

If chromic acid is titrated with standard alkali, two points of inflection of pH are observed, one around pH 4 and one around pH 8.2. Chromic acid can then be considered as a dibasic acid ionising stepwise thus:

$$H_2CrO_4 \rightarrow \overset{+}{H} + H\overset{-}{C}rO_4$$

$$H\overset{-}{C}rO_4 \rightarrow \overset{+}{H} + \overset{--}{CrO_4}$$

The idea of the dichromate ion will not invalidate this simplified picture since the dichromate ion can be considered as simply a dehydrated $H\overset{-}{C}rO_4$ ion.

$$2\ H\overset{-}{C}rO_4 \rightarrow \overset{--}{Cr_2O_7} + H_2O$$

When titrating chromic acid to the first point of inflection of pH (assume pH 4), chromic acid may be considered as a monobasic acid, i.e., with only one replaceable hydrogen ion.

$$H_2CrO_4 + \overset{-}{OH} \rightarrow H_2O + H\overset{-}{C}rO_4$$

Every equivalent of zinc oxide mixed with the chromate will mean an equivalent less of alkali required to back titrate to the point of inflection around a pH of 4. It then becomes possible, knowing the chromate concentration, to calculate the equivalent zinc oxide. Such titrations were carried out with the five samples containing 0, 0.5, 1.0, 2.0, 4.0% ZnO. The procedure was to take a 1 gram sample, add 30 ml of ± N/3 H_2SO_4 and warm until the zinc yellow was completely dissolved. Cool, dilute to ±200 ml., and backtitrate with ± N/3 NaOH to two inflections in the pH curve. The pH was measured with a glass - calomel electrode system. The second point of inflection was also measured in most cases but no use was made of it in the calculations. Since precipitation always started between the first and second points of inflection, the position of the second point of inflection would be influenced by how much chromate and zinc were taken out of solution. Equilibrium conditions were probably not established which would also tend to make the second point of inflection a variable. At any rate, nothing could be done with the second point of inflection but it is included in the data for the sake of completeness.

Following are some typical calculations to illustrate the methods

Sample Y-232-D Lot 93266

Zinc Yellow with 0% ZnO added

By analysis, chromate as CrO_3 = 41.12%

$\frac{0.4112}{0.1}$ = 4.112 milliequivalents CrO_3 per gram (as a mono-basic acid)

A 1 gram sample dissolved in 30 ml of 0.3899N H_2SO_4 required 13.3 ml of 0.3816N NaOH back titration to the first point of inflection of pH.

30 x 0.3899	=	11.697	milliequivalence of H_2SO_4 added
13.3 x 0.3816	=	5.076	" " NaOH backtitrated
		6.621 %	
	-	4.112 %	" due to chromate
		2.509 %	" attributable to ZnO

Milliequivalent Wt. of ZnO = 0.04069

100 x 2.509 x 0.04069 = 10.21% ZnO

The figure 10.21% ZnO is then the calculated ZnO basicity of the pigment with no zinc oxide present. If it gets much above this, free zinc oxide may be present.

Sample Y-232-D Lot 93266

Zinc Yellow + ZnO dry ground into it to the extent of 4.0% ZnO

Chromate = 39.48% CrO_3

Same procedure used as for above sample.

Back titration = 11.65 ml

		11.697	
11.65 x 0.3816	=	4.444	
		7.251	
		-3.948	
		3.303 x 4.069	= 13.44% ZnO
			-10.21
			3.23% ZnO

The amount of ZnO in excess of that expected for a typical zinc yellow was 3.23% ZnO. This when compared to 4% is not a good check but the precision of the method is admittedly poor, the purpose being simply to indicate the possible presence of free zinc oxide.

For other samples the procedure was sometimes modified to the extent of using sample weights other than 1 gram and varying the amount of standard sulfuric acid used to dissolve the sample.

Table II shows all of the data for all samples titrated. Graphs 1 and 2 show typical titration curves for zinc yellow and zinc yellow - zinc oxide mixtures.

TABLE II

COMPILED DATA FOR THE BASICITY DETERMINATION OF ZINC YELLOW AND RELATED PIGMENTS

Sample Designation	Sample Weight in grams	Chromate as % CrO_3	Milli-equivalent of H_2SO_4	Back Titration milliequivalent of NaOH 1st inflection at pH ± 4	Back Titration milliequivalent of NaOH 2nd inflection at pH ± 8	Basicity expressed as % ZnO	% ZnO in excess of that in typical zinc yellow
Y-232-D Lot 93266 + 0% ZnO	1	41.12	11.697	5.076	16.49	10.21	0.0
" + 0.5% ZnO	1	40.91	11.697	4.960	16.41	10.76	0.55
" + 1.0% ZnO	1	40.42	11.697	4.922	16.53	11.12	0.91
" + 2.0% ZnO	1	40.30	11.697	4.770	16.45	11.80	1.59
" + 4.0% ZnO	1	39.48	11.697	4.446	16.33	13.44	3.23
Reichhold's Zinc Yellow 1420 (C-46530)	4	42.92	41.17	11.28	58.35	12.93	2.61
Reichhold's Zinc Yellow 12062 (C-46632)	4	42.59	34.31	5.99	51.61	11.47	1.26
Unknown Mfg. From W. P. Fuller (C-45839)	5.005	41.18	51.26	10.50		16.38	6.17
Kentucky's zinc yellow 2813 (C-46380)	4	45.14	34.31	6.43		9.99	-0.33
Zinc trioxychromate (927-77A)	2.006	20.06	34.1[illegible]	5.74		49.48	
Zinc tetraoxychromate (927-46-D)	1	17.17	17.07	1.75		55.34	

DISCUSSION OF DATA OF TABLE II

As seen from the data in the first row a typical zinc yellow has a basicity of 10.21% ZnO. The theoretical percent assuming the formula 3 $ZnCrO_4 \cdot K_2CrO_4 \cdot ZnO \cdot 3H_2O$ is only 9.32% ZnO. This may indicate that a small amount of a more basic zinc chromate is also present which is a reasonable supposition since more basic zinc chromates do exist. The results in the last column make the assumption that 10.21% ZnO represents a typical basicity for zinc yellow in spite of the 9.32% theoretical figure. The knowledge of this assumption decreases the quantitative significance of the data in the last column because a mixture of zinc yellow with a more basic zinc chromate such as the trioxychromate will very noticably increase the basicity without adding any ZnO. The high basicity of more basic zinc chromates is indicated in the last two rows. Assuming zinc trioxychromate as $ZnCrO_4 \cdot 3ZnO \cdot 3H_2O$, the theoretical basicity is 50.92% ZnO. The observed figure of 49.4% is in fair agreement and is obviously much higher than 10.21% which is that for a typical zinc yellow. X-ray diffraction of a typical zinc trioxychromate showed no ZnO.

Assuming zinc tetroxychromate as $ZnCrO_4 \cdot 4ZnO \cdot 4H_2O$, the theoretical basicity becomes 56.23% ZnO. The observed figure of 55.34 is also in fair agreement. Here though, ZnO was found by X-ray diffraction analysis when examining a typical zinc tetroxychromate so at least part of the basicity can be attributed/free zinc oxide.

Comparing X-ray diffraction results on Reichhelds 1420 (C-46530) with the basicity results gives 1.0% against 2.16% ZnO. This is in better agreement than the results on C-45839, where the comparison is 1.5% as against 6.17% ZnO. Since the series where zinc oxide was ground into the sample had a tendency to give basicity figures on the low side, the high results when comparing the competative samples lends support to the idea that the samples contain more basic zinc chromates in addition to free zinc oxide. It also lends evidence to the idea that the zinc oxide in these pigments was not ground into the pigments but that the pigments were prepared under such conditions of basicity that not only was a more basic zinc chromate pigment produced but some free ZnO was also left in the pigment. Failure to observe any fluorescence in these pigments also tends to show that the free ZnO was introduced in some manner other than dry mixing.

NOTE BOOK REFERENCES

NB 1014 p. 4 - 12
Zinc oxide ground into zinc yellow. These and competative samples titrated with acid and alkali.

NB 1048 p. 66
Fluorescent method used.

NB 1013 p. 144
A competitive sample, a zinc trioxychromate, and a tetroxychromate titrated with acid and alkali.

CORRESPONDENCE

J. B. Nichols to A. R. Hanke (11/13/42)
Samples of zinc oxide ground into zinc yellow examined with X-ray diffraction.

J. B. Nichols to A. R. Hanke (12/17/42)
Competitive samples and N# samples examined with X-ray diffraction.