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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

Final Report

ELECTRON DIFFRACTION STUDIES
PART II - APPLICATIONS

Period Covered:
JUNE 1944 - APRIL 1945

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Final Report

Title: ELECTRON DIFFRACTION STUDIES
PART II - APPLICATIONS

Period Covered: JUNE 1944 - APRIL 1945

SUBMITTED BY: F. KARUSH F. Karush DATE SUBMITTED: 1-2-47

APPROVED BY: B. H. PERKINS B. H. Perkins DATE ISSUED: 1-14-47

INTRODUCTION

This report presents a description of the application of the electron diffraction camera to pigment problems. The camera itself is described in Part I, KN-46-76, which also includes the procedure for the preparation of diffraction mounts and for the measurement of the diffraction patterns. In the work presented here the attempt was made to apply the diffraction technique to various types of pigments. While this technique is particularly suitable for studying thin surface films, its utility in the identification of the crystal structure of pigments was also investigated. This appeared desirable because some pigments have a particle size small enough to yield satisfactory patterns. Furthermore, in some cases the particle size may be even too small to yield a useful x-ray diffraction pattern and yet may give an excellent electron diffraction pattern.

SUMMARY AND CONCLUSIONS

1. Medium ($PbCrO_4$) and light yellows ($PbCrO_4$ & $PbSO_4$) yield satisfactory electron diffraction patterns. All patterns of samples of these pigments are usually identical and agree satisfactorily with the x-ray diffraction pattern of monoclinic lead chromate with respect to the values of the interplanar spacings. However, significant differences in relative intensities between the x-ray and electron diffraction patterns are observed. This can be largely attributed to the effect of the orientation of the needle-shaped particles in the electron diffraction mount. If a more symmetrically shaped chrome yellow is used, a pattern is obtained which shows the same ring diameters as the usual electron diffraction pattern but considerably different relative intensities.

2. The electron diffraction method is not suitable for the study of the phase composition of such systems as $PbCrO_4$ - $PbSO_4$ and $PbCrO_4$ - $Pb_3(PO_4)_2$. The patterns are often of poor quality and like that of $PbCrO_4$ are quite complicated. X-ray diffraction is a much more satisfactory method for this purpose.

3. Treatment of lead chromate with as little as 1% sodium stearate gives rise to a new set of rings in the diffraction pattern together with some faint rings from the $PbCrO_4$ pattern. This means that it is possible to detect and study mono-molecular layers of long chain compounds on $PbCrO_4$ and probably other pigments.

4. Electron diffraction does not afford positive evidence for the coating of $PbCrO_4$ with aluminum hydrate, probably because the latter is amorphous and does not give rise to distinctive rings in the diffraction pattern.

5. All iron blues examined, including B-57-D, B-66-D, B-197-D and B-216-D, gave identical electron diffraction patterns, showing that they have the same crystal structure. Because of the excellent quality of the iron blue pattern and the symmetry of the iron blue structure (face-centered cubic, length of cube 10.2 angstroms), it is used to determine the instrumental constant of the diffraction camera. This constant permits the easy conversion from ring diameters to interplanar spacings.

Attempts to detect the presence of adsorbed layers of stearate and Fixanol on iron blue have been unsuccessful. This is probably due either to the original absence of such layers or their ready removal in the course of preparing the diffraction mount.

6. Electron diffraction patterns of a series of barium lithols and duols show at most some variation of relative intensities but a constancy of the ring diameters. This means that duolization does not involve a crystal structural change of this pigment.

7. A series of samples, prepared by diazotizing and coupling Red 2B Acid (o-chlor-p-toluidine-m-sulfonic acid) with beta naphthol and precipitating with strontium and calcium in various ratios, showed almost identical patterns. Substitution of one metal by the other apparently leaves the structure unchanged. A typical pattern is shown in Fig. 4D.

8. The study of coalesced phthalocyanines, including BX-CR (TiO_2 + CPC) did not lead to any unequivocal results. Only in the case of phthalocyanine coalesced with zinc oxide did the diffraction pattern indicate coating of the oxide by the colored pigment.

9. Samples of Lake Red S (p-toluidine-m-sulfonic acid → BON, Ba, rosinated) made with use of either bicarbonate, soda ash or alkali gave diffraction patterns which showed that the samples possessed identical crystal structures. Pattern A of Fig. 5 is typical of these.

10. The electron diffraction method often can be used to distinguish and identify structurally similar organic yellow pigments. Identity of diffraction patterns does not, however, always mean identity of composition as illustrated by the fact that dichlorbenzidine diazotized and coupled to acetoacetanilide gives a compound with a pattern identical to that from the compound obtained by coupling with acetoacet-meta-xylidide.

11. It is clear from the results of this study that in many cases the electron diffraction technique can yield information, otherwise unavailable, which may be useful in the solution of specific pigment problems. The possible utility of this technique depends upon the particular problem under consideration and must be evaluated for each

case. Because the electron diffraction method is particularly suitable for studying surface films, it appears desirable to continue the exploratory investigation of adsorbed layers on pigment particles with this method.

SUMMARY OF EXPERIMENTAL DETAILS

Unless otherwise noted the diffraction patterns presented here have been obtained using 40 kilovolt electrons. The prints exhibited in this report represent 2-fold magnifications of the original patterns. The exposure time for each print has been varied for the various groups of rings to make visible all the rings which can be seen in the negative. Thus the actual relative intensities are not faithfully reproduced in the prints.

A. Chrome Yellows

Medium and light yellows belong to the monoclinic system and are usually needleshaped. A typical pattern for this group is given in B of Fig. 1. This is the pattern of a light yellow (Y-2034, lot 7645), an electron micrograph of which is shown in Fig, 2, B. The uniqueness of this pattern depends to a large extent on the shape of the pigment particles. If another pigment of identical composition but of different shape is used, shown in Fig, 2, A, a pattern quite different in appearance is obtained. This pattern is shown in Fig. 1, A and actually differs from B only in the relative intensities of the rings. This difference arises from the fact that asymmetric particles assume a preferred orientation when mounted for electron diffraction or electron microscopy. This is evident from Fig. 2, B where practically all the needles lie in the plane of the paper. The orientation of crystals in a diffraction mount can also be detected by changing the angle of incidence between the electron beam and the film supporting the pigment particles from 90° to another angle, e.g. 45°. This was done in the case of a sample of lead chromate and the pattern obtained is shown in Fig. 1, C. It is seen that instead of continuous rings two or more arcs appear, thus furnishing unequivocal evidence of preferred orientation.

In Table I is given a comparison of the electron diffraction data from the pattern of Fig. 2, A with x-ray diffraction data of monoclinic lead chromate. It is seen that there is satisfactory agreement with respect to the values for the interplanar spacings. However, significant differences exist in the values of the relative intensities. To what extent this can be attributed to orientation effects is not known.

An effort was made to determine if the electron diffraction technique could be used to study the phase composition of the systems $PbCrO_4$ - $PbSO_4$ and $PbCrO_4$ - $Pb_3(PO_4)_2$, as well as to observe any surface effect in these mixtures. $Pb_3(PO_4)_2$ gives a fairly satisfactory pattern, shown in Fig, 3,A but that of $PbSO_4$ is quite poor. The pattern in

Fig. 3, B is that of a sample containing 40% $PbCrO_4$ and 60% $Pb_3(PO_4)_2$, coprecipitated. It illustrates the complicated patterns obtained from such mixtures and indicates the excessive difficulty in attempting to make quantitative estimates of phase composition. For purposes of comparison, a pattern of monoclinic $PbCrO_4$ is shown in Fig. 3, C. It is quite clear that this technique is unsuitable for studying the above systems.

Samples of $PbCrO_4$ containing up to 12% aluminum hydrate were examined but unequivocal evidence for the presence of the hydrate on the pigment surface could not be found. One reason for this is probably that the hydrate is amorphous and consequently does not give rise to any distinctive rings. With samples of $PbCrO_4$ which had been treated with aluminum hydrate and boiled, a slight but definite change in the relative intensities of the rings of the $PbCrO_4$ pattern was observed. The precise significance of this result has not been established.

Studies with stearate-treated $PbCrO_4$ gave very encouraging results with respect to the study of organic surface treatments. It was found, for example, that a sample of $PbCrO_4$ treated with as little as 1% of sodium stearate in the slurry gave rise to a new set of strong rings with the $PbCrO_4$ rings only faintly apparent. A pattern of such a sample (989-36B) is shown in Fig. 3, D and is to be compared with the pattern of untreated $PbCrO_4$ just above it. On the assumption that the long stearate chain is oriented perpendicularly to the crystal face and the specific surface of the $PbCrO_4$ is 5 square meters per gram, it can be calculated that a monomolecular layer of stearate requires approximately 1% of sodium stearate. It seems very likely that such a monomolecular layer is responsible for the new rings and greatly reduces the diffraction by the $PbCrO_4$. The use of 2.5% sodium stearate gives about the same pattern. The data from such a pattern (223c) are given in Table II which lists the ring diameters, corresponding interplanar spacings and relative intensities and the identification of the rings in terms of $PbCrO_4$ or stearate.

Mechanical mixtures of $PbCrO_4$ and either sodium stearate or lead stearate were used as controls. With as much as 2-1/2% of stearate the patterns of these controls were essentially equivalent to that of $PbCrO_4$ with indication of the strongest ring of the Pb stearate pattern. The pattern obtained from Pb stearate itself is the same as the set of new rings appearing in stearate treated $PbCrO_4$. The choice of the medium in which the sample is dispersed is very important with respect to the appearance of the stearate rings in treated $PbCrO_4$. Amyl acetate is satisfactory in this respect but when mixed with butyl or methyl alcohol the stearate rings are hardly apparent. Ethyl acetate is also objectionable on this account as is also the presence of even a slight amount of nitrocellulose in the dispersion.

B. Iron Blues

Of all the pigments studied, iron blues yield by far the best electron diffraction patterns. This is because of their small particle size, making them transparent to electrons, and their highly symmetrical structure (face-centered cubic). A typical iron blue pattern is shown in Fig. 4, A and is given by all iron blue pigments examined, including B-57-D, B-66-D, B-197-D and B-216-D. Since the lattice constant of iron blue is accurately known, 10.2 Angstroms, this pattern can be used to obtain the calibration constant for the apparatus. This constant is used to convert ring diameters into interplanar spacings. The data involved in the calculation of this constant are included in Table III which lists 28 ring diameters, their relative intensities and the corresponding values of h, k, l and the interplanar spacings. Satisfactory iron blue patterns can be obtained with 20 KV electrons.

Attempts were made to detect the presence of surface coatings on iron blue samples treated with sodium stearate or Fixanol. Even when as much as 30% of one of these agents was used no evidence of an adsorbed organic layer was observed. The slight addition to the pattern was what might be expected from a mechanical mixture. It is still unknown whether these agents were not originally adsorbed by the pigment or whether they were removed from the surface in the course of the mounting procedure. In this connection it should be mentioned that ethyl acetate was used as the dispersion medium. In view of the behavior with stearate treated $PbCrO_4$ it is not unlikely that this solvent would remove an adsorbed film of stearate or Fixanol.

C. The "Duol" Effect

The effect of rosin on a barium lithol (2-naphthylamine sulfonic acid → BN, Ba) was investigated by the electron diffraction technique. Samples (1127-22 series) which contained varying amounts of rosin up to 165 grams per mole of color (mol. wt. 515.4), and subjected to temperature treatments ranging from room temperature to boiling for more than one hour, were studied. The only change observed occurred with a sample containing 11 grams of rosin per mole of color which had been boiled for 2 to 4 minutes. The pattern of this sample is shown in Fig. 4, C and is to be compared to B in Fig. 4. The latter is the pattern obtained from lower temperature samples of the same rosin content. Curiously enough, it is also the pattern found with all samples with less than 11 grams of rosin as well as more rosin, regardless of the heat treatment. Close examination reveals that patterns B and C of Fig. 4 differ only in relative intensities. It seems unlikely, therefore, that duolization involves any crystal structural change of the color. It may be added that barium rosinate itself gives no diffraction rings.

D. Organic Yellows

The possibility of the identification of structurally similar organic pigments was investigated by a study of the diffraction patterns of a series of organic yellow toners. Good examples of such

patterns are shown in Fig. 5, B and C. B is the pattern of a competitive pigment (C#-47935) and is identical with the pattern obtained from the product prepared by coupling dichlorbenzidine with acetoacet-meta-xylidide. A very interesting series of patterns is obtained from the yellows prepared by coupling dichlorbenzidine with acetoacetanilide, acetoacet-meta-xylidide, acetoacet-2CH_3-5CH_3O-anilide and acetoacet-2,5$(CH_3O)_2$-anilide respectively. The patterns of these substances are shown in Fig. 6, A, B, C and D respectively. The introduction of two methyl groups into acetoacetanilide apparently leaves the crystal structure unaltered as a comparison of patterns A and B indicates. However, if one methyl group and one methoxy group are introduced, a definite change in structure results, as seen in pattern C. The use of two methoxy groups does not lead to any further alteration of structure as indicated by the identity of patterns C and D.

In the case of para-chlor-ortho-nitro-aniline coupled to acetoacetanilide, acetoacet-ortho-toluidide and acetoacet-meta-xylidide respectively, the crystal structure is more sensitive to substitution in the second component than it is in the case of the dichlorbenzidine series. This is clear from the fact that the pattern of these three products, shown in Fig. 7, B, C and D, differ from one another. A pattern of the standard Hansa Yellow toner, YT-445-D (meta-nitro-para-toluidine → acetoacetanilide) is given in Fig. 7, A.

TABLE I.

Comparison of electron diffraction data (258B) and x-ray diffraction data for monoclinic $PbCrO_4$.

X-ray data from Ind. & Eng. Chem. 10, 489(1938)

Ring No.	Ring diam. in cm.	ELECTRON DIFFRACTION Interplanar spacing in A	ELECTRON DIFFRACTION Relative intensity	X-RAY Interplanar spacing in A	X-RAY Relative intensity
1	0.89	4.96	0.20	4.97	0.23
2	1.02	4.34	0.27	4.38	0.46
3	1.20	3.69	0.20	3.75	0.11
4	1.36	3.25	0.70	3.28	1.00
5	1.48	2.99	1.00	3.01	0.86
6	1.64	2.70	0.34	2.71	0.11
7	1.75	2.53	0.55	2.53	0.11
8	1.91	2.32	0.27	2.32	0.11
9	1.98	2.23	0.27	2.25	0.34
10	2.24	1.97	0.45	1.97	0.40
11	2.40	1.84	0.45	1.85	0.34
12	2.77	1.60	0.27	1.61	0.06
13	2.87	1.54	0.20	1.54	0.06
14	3.02	1.46	0.20	1.42	0.09
15	3.19	1.39	0.27	-	-
16	3.29	1.34	0.20	-	-
17	3.35	1.32	0.20	-	-
18	3.45	1.28	0.27	-	-
19	3.61	1.22	0.20	-	-
20	3.80	1.16	0.20	-	-
21	3.95	1.12	0.20	-	-
22	4.12	1.07	0.20	-	-
23	4.45	1.00	0.20	-	-

TABLE II.

Electron diffraction data from pattern of $PbCrO_4$ treated with 2-1/2% Na stearate(pattern no. 2230.)

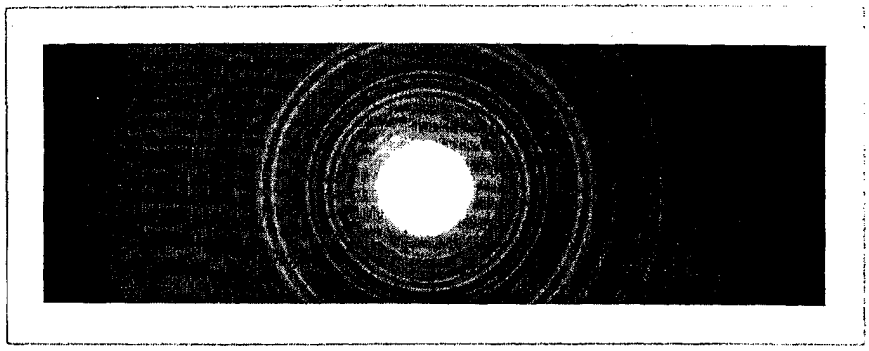
Ring No.	Ring diameter in cm.	Interplanar spacing in Angstroms	Relative Intensity	Identification
1	0.87	5.08	0.22	$PbCrO_4$
2	1.06	4.16	1.00	Stearate
3	1.20	3.68	0.70	Stearate
4	1.34	3.30	0.22	$PbCrO_4$
5	1.45	3.05	0.46	$PbCrO_4$
6	1.77	2.50	0.37	Stearate
7	1.94	2.28	0.22	$PbCrO_4$
8	2.02	2.19	0.28	Stearate
9	2.14	2.06	0.16	Stearate
10	2.22	1.99	0.16	$PbCrO_4$
11	2.38	1.86	0.26	Stearate $PbCrO_4$
12	2.65	1.67	0.16	$PbCrO_4$
13	2.74	1.614	0.16	$PbCrO_4$
14	2.83	1.563	0.16	$PbCrO_4$
15	3.08	1.435	0.16	$PbCrO_4$

TABLE III.

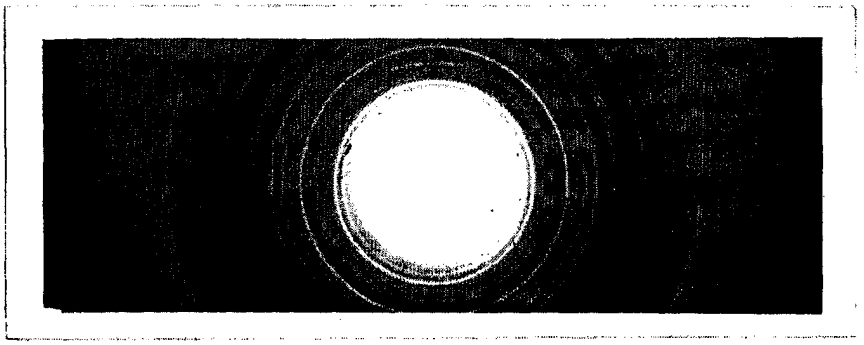
Calculation of conversion constant from diffraction pattern of iron blue (181C.)

$K = \frac{\text{Å}^\circ \, D_{hkl}}{\sqrt{h^2+k^2+l^2}}$ $\qquad d = \frac{A^\circ}{\sqrt{h^2+k^2+l^2}}$ $\qquad$ Å° = 10.2A°

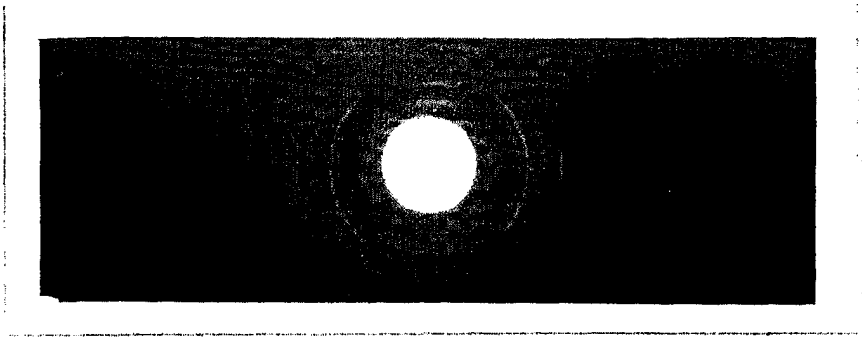
Ring No.	Ring diam. in cm, D.	Relative intensity	h k l	$h^2+k^2+l^2$	$\sqrt{h^2+k^2+l^2}$	Interplanar spacing in angstroms, d	Conversion constant, K in cm-A°
1	0.75	0.24	111	3	1.732	5.89	4.42
2	0.86	0.60	200	4	2.000	5.09	4.38
3	1.22	1.00	220	8	2.828	3.60	4.40
4	1.43	0.14	311	11	3.317	3.08	4.40
5	1.50	0.60	222	12	3.464	2.94	4.42
6	1.72	0.72	400	16	4.000	2.55	4.38
7	1.93	0.86	420	20	4.472	2.28	4.40
8	2.12	0.19	422	24	4.899	2.08	4.41
9	2.46	0.72	440	32	5.657	1.80	4.43
10	2.59	0.60	600 442	36	6.000	1.70	4.40
11	2.72	0.72	620	40	6.325	1.61	4.38
12	2.86	0.14	622	44	6.633	1.54	4.44
13	3.01	0.19	444	48	6.928	1.47	4.42
14	3.12	0.72	640	52	7.211	1.41	4.40
15	3.25	0.60	642	56	7.483	1.36	4.42
16	3.57	0.50	820 644	68	8.246	1.24	4.42
17	3.68	0.50	822 660	72	8.485	1.20	4.42
18	3.77	0.24	662	76	8.718	1.17	4.41
19	3.88	0.24	840	80	8.944	1.14	4.42
20	4.06	0.40	664	88	9.381	1.09	4.42
21	4.32	0.24	860 1000	100	10.000	1.02	4.45
22	4.41	0.40	862 1020	104	10.20	1.00	4.41
23	4.50	0.24	666 1022	108	10.39	0.982	4.42
24	4.67	0.40	864 1040	116	10.77	0.948	4.42
25	4.75	0.24	1042	120	10.95	0.932	4.40
26	4.98	0.19	1044	132	11.49	0.887	4.42
27	5.07	0.32	866 1060	136	11.66	0.875	4.44
28	5.30	0.32	1220	148	12.17	0.838	4.44



A
Pattern No. 258B
light yellow
Y-2034-D(lot 7634)



B
Pattern No. 258C
light yellow
Y-2034-D(lot 7645)



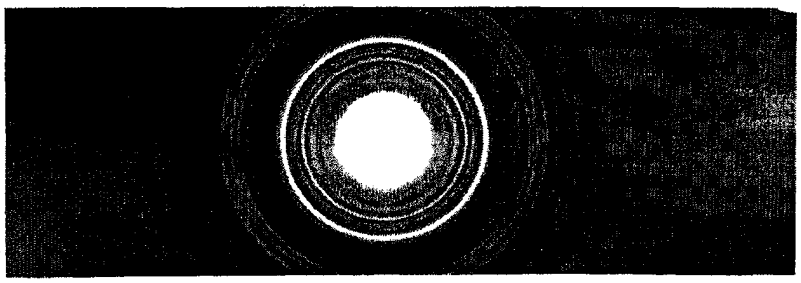
C
Pattern No. 301C
$PbCrO_4$
($1134\text{-}18A_1$)

FIG. 1

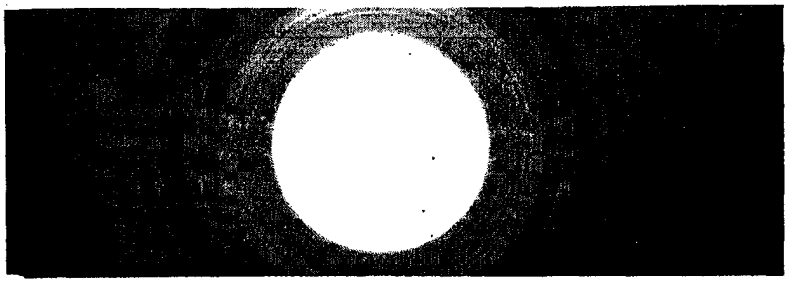
A.
light yellow
Y-2054-D(lot
1137-2-10
mag. 25000 x

B
light yellow
Y-2034-D(lot
1137-2-9
mag. 25000 x

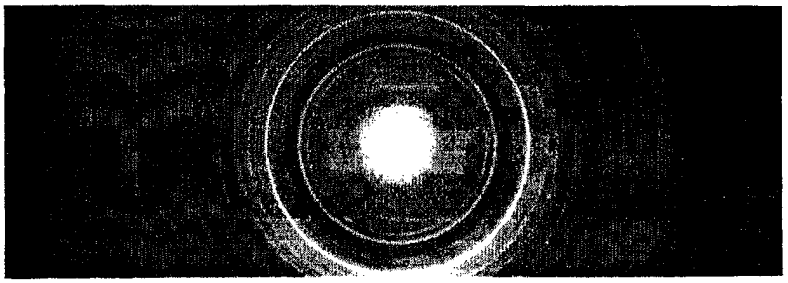
FIG. 2.



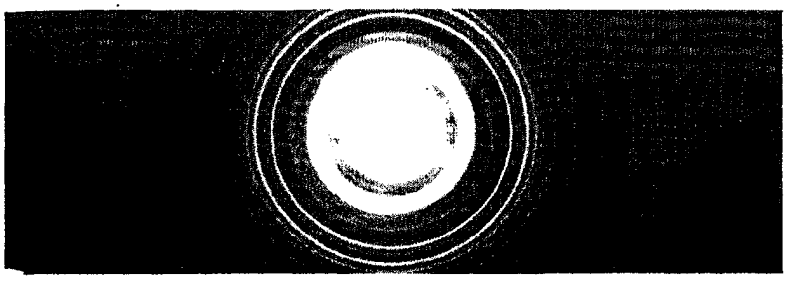
A
Pattern No. 187C
$Pb_3(PO_4)_2$
(969-46F1)



B
Pattern No. 200C
40% $PbCrO_4$ + 60%
$Pb_3(PO_4)_2$ (969-46D)

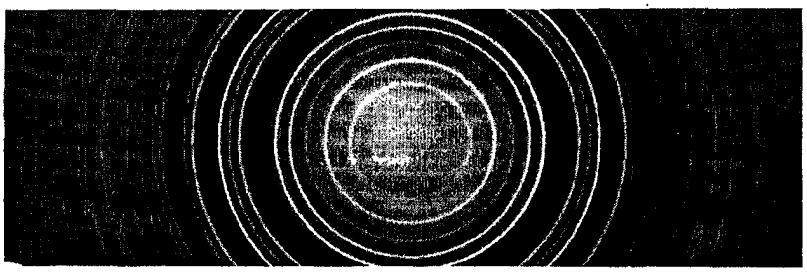


C
Pattern No. 222B
$PbCrO_4$
(969-46A)

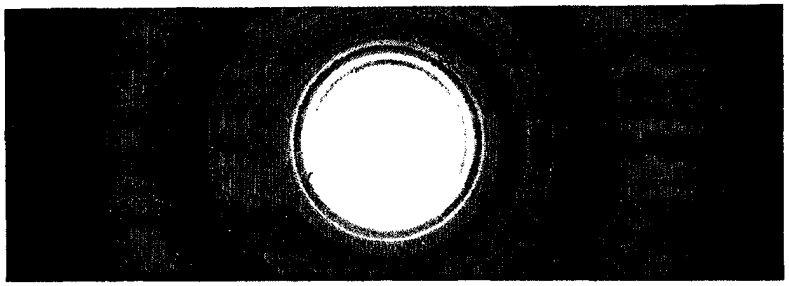


C
Pattern No. 171C
$PbCrO_4$ + 1% Na Stearate
(969-36D)

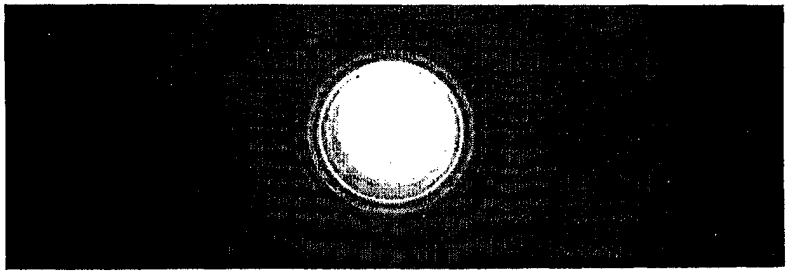
FIG. 3



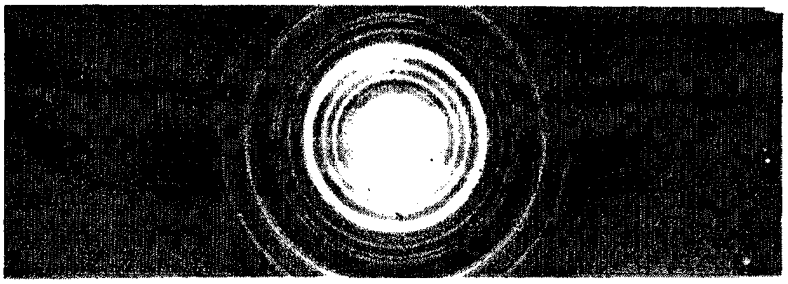
A
Pattern No. 298A
iron blue
(C# 47628)



B
Pattern No. 298B
Ba lithol
(1127-22A$_3$)

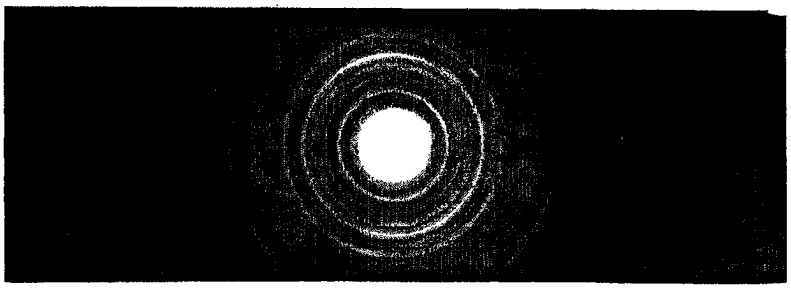


C
Pattern No. 304A
Ba lithol + 1.1% rosin/mole, boil 2 to 4 mins.
(1127-22B$_4$)

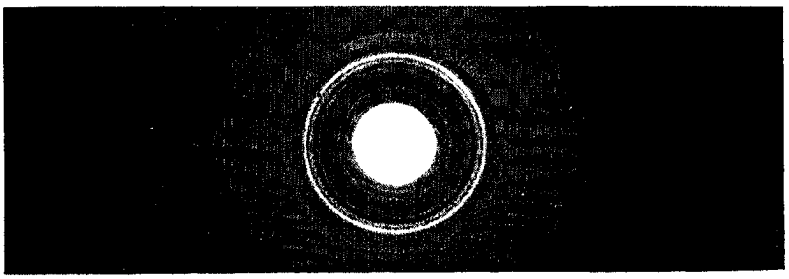


D
Pattern No. 299A
Red 2B → BON, 13% Ca, 87% Sr
(1143-14E)

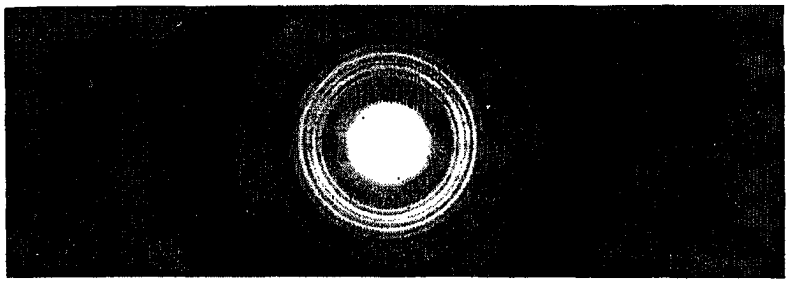
FIG. 4



A
Pattern No. 231A
PTMSA → BN, Be
(1108-25E)

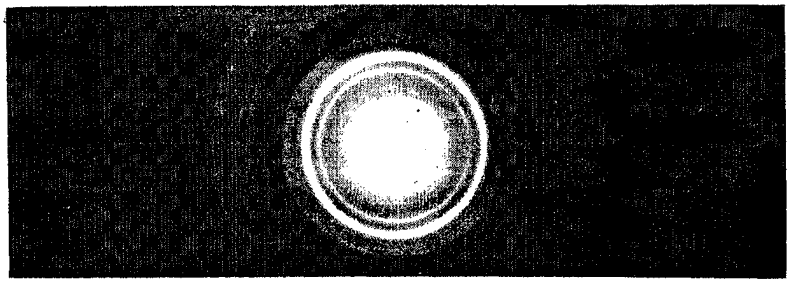


B
Pattern No. 316B
organic yellow toner
(C#-47965)

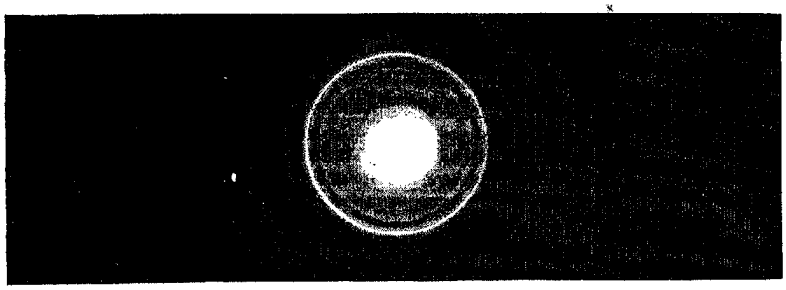


C
Pattern No. 256B
DC1B → AAo-anisidide
(946-18E)

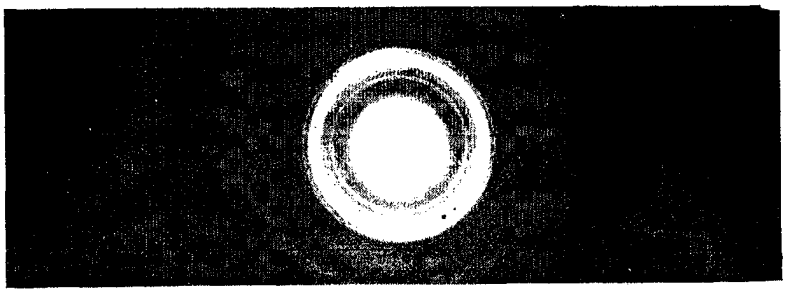
FIG. 5.



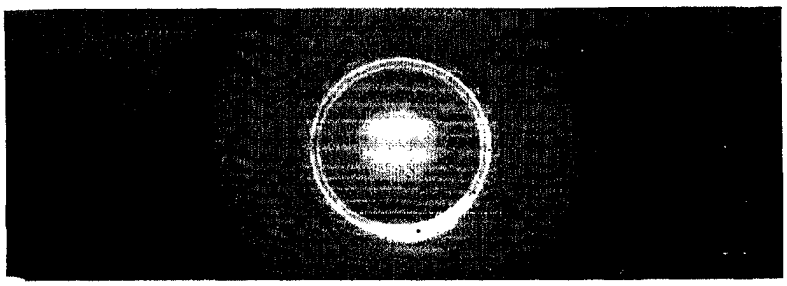
A
Pattern No. 248A
DC1B → AAA
(1095-31A$_1$)



B
Pattern No. 248B
DC1E → AA-m-X
(1095-31B$_1$)

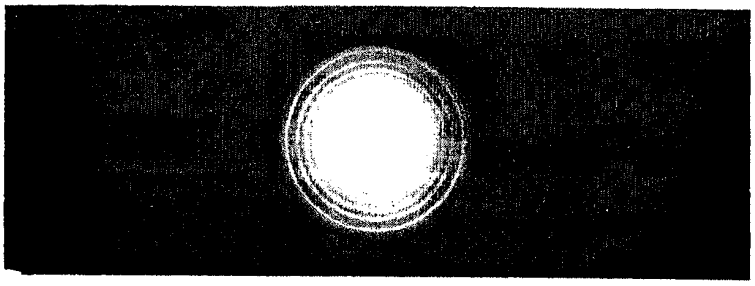


C
Pattern No. 248C
DC1B → AA-2CH_3-5CH_3O-A
(1095-31C$_1$)

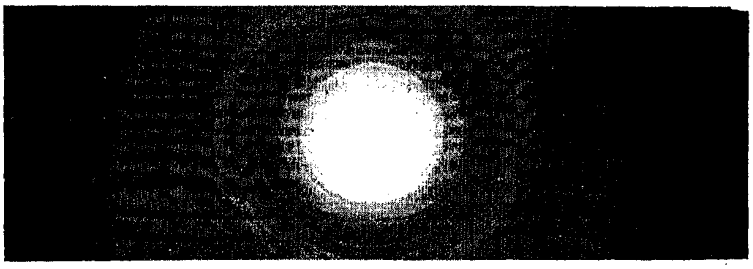


D
Pattern No. 249A
DC1B → AA-3,5$(CH_3O)_2$-A
(1095-31D$_1$)

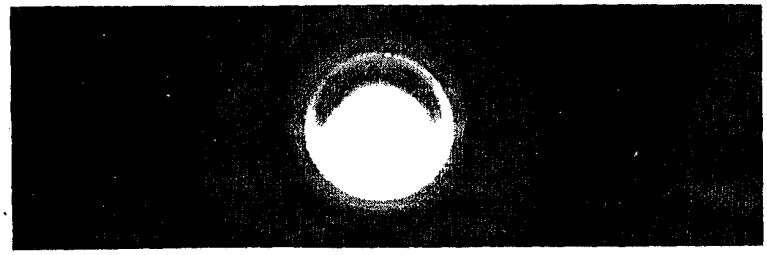
FIG. 6



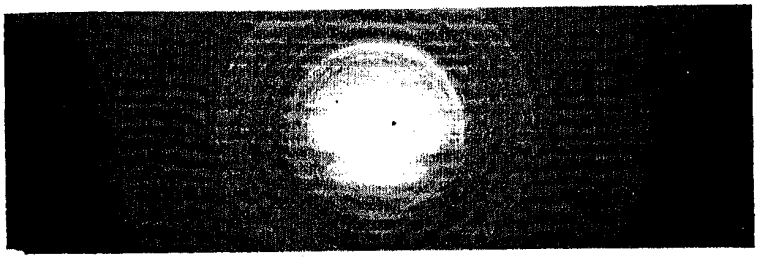
A
Pattern No. 242C
Hansa Yellow
YT-445-D



B
Pattern No. 243A
PCONA → AAA
(1003-38A$_1$)



C
Pattern No. 243B
PCONA → AA-o-T
(1003-38B$_1$)



D
Pattern No. 243C
PCONA → AA-m-X
(1003-38C$_1$)

FIG. 7