



Standard Test Method for Identification of Crystalline Pigments and Extenders in Paint by X-Ray Diffraction Analysis¹

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1. Scope

1.1 This test method covers the identification of crystalline pigments and extenders in liquid paint and dry paint film. It is applicable to both water-reducible and solvent-reducible paint. It also may be used to identify pigment and extender in grind paste or alone as dry powder. It is not applicable to amorphous components such as carbon black, amorphous silica, or highly processed clay.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Section 6.

2. Referenced Documents

2.1 ASTM Standards:

D 3925 Practice for Sampling Liquid Paints and Related Pigmented Coatings²

3. Summary of Test Method

3.1 Every crystalline substance, in this case pigment or extender, has a characteristic X-ray diffraction pattern. Whether the substance is present alone or in a mixture, it produces its pattern independently and can be identified by it. An X-ray diffraction pattern of a sample is recorded. Each crystalline substance in the sample is identified by the Hanawalt or Fink method or other systematic procedure based on comparison of the diffraction pattern of the sample with reference patterns of standards.^{3,4,5}

4. Significance and Use

4.1 The choice of pigments and extenders influences the appearance, durability, cost, and other properties of paint. This

test method is a convenient way, and probably the most reliable, to identify pigments in paint.

5. Apparatus

5.1 *X-ray Diffractometer*, suitable for collecting intensity versus two theta (2θ) angle diffraction patterns in the range from 5° to $65^\circ 20$. It is preferred that the diffractometer be equipped with a copper target X-ray tube and a monochromator that passes only copper K-alpha radiation. If a monochromator is not available, then a suitable filter may be used to remove copper K-beta radiation from the diffracted X-ray beam. A nickel filter may be used for this purpose when a copper target tube is employed.

NOTE 1—Follow the recommendations of the manufacturer of the diffractometer used.

5.2 *Liquid Paint or Grind Paste:*

5.2.1 *Paint Shaker.*

5.2.2 *Film Applicator*, that will produce a 3- to 10-mil (75- to 250 μm) wet film thickness.

5.2.3 *Plastic Sheet*, such as polyester film, that contains no crystalline components that would produce interfering X-ray diffraction peaks and is not attacked by paint solvent.

5.2.4 *Perforated Suction Plate* or other flat surface.

5.3 *Paint Chips or Pigment Powder:*

5.3.1 *Miniature Reciprocating Ball Mill.*

5.3.2 *Stainless Steel Vials*, with agitator for ball mill.

5.3.3 *Powder Specimen Holders*, for X-ray diffractometer.

6. Hazards

6.1 *Precaution*—As exposure to excessive quantities of X-radiation is injurious to health, X-ray producing equipment can be dangerous to both the operator and persons in the immediate vicinity unless safety precautions are strictly observed. Therefore, users should avoid exposing any parts of their bodies, not only to the direct beam, but also to secondary or scattered radiation that occurs when an X-ray beam strikes or passes through any material. It is strongly recommended that users check the degree of exposure by film carried on them or by the use of dosimeters and that blood counts be made periodically. Before utilizing the equipment, all persons designated or authorized to operate X-ray instrumentation or supervise its operation, should have a full understanding of its nature and should also become familiar with established safe exposure

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² *Annual Book of ASTM Standards*, Vol 0.6.01.

³ *Search Manual*, (Hanawalt), "Inorganic Phases," International Centre for Diffraction Data, (ICDD), Catalog No. HA 42, Newtown Square Corporate Campus, 12 Campus Blvd., Newtown Square, PA 19073-3273.

⁴ *Search Manual*, (Fink), "Inorganic Phases," ICDD.

⁵ "Powder Diffraction File, Inorganic," ICDD.

factors by a careful study of the NIST handbook,⁶ “X-ray Recommendations of the International Roentgen Ray Committee on X-ray Protection,” the manufacturer’s instruction manual, and other standard publications on the subject. Inquiries should be made of state agencies as to existing requirements.

7. Specimen Preparation

7.1 Prepare a specimen from the sample using one of the following methods:

7.1.1 *Liquid Paint or Pigment Paste*—Thoroughly mix and sample the paint or paste in accordance with Practice D 3925. Place a plastic sheet on the perforated suction plate. On the sheet make a drawdown of the sample. A wet film thickness of 3.0 to 10.0 mil (75 to 250 μm) is suggested. Cut from the drawdown on the plastic sheet a specimen of shape and size suitable for the mounting in the specimen holder of the diffractometer.

7.1.2 *Paint Chip*—Using a ball mill, grind to a powder the paint chip or, if it contains more than one layer, the part of the chip of interest. Prepare sufficient specimen to fill the specimen holder or to satisfy the requirements of the preparation technique to be used. In cases where the chip has a planar surface and uniform thickness, it may be possible to cut the chip to the required dimensions and mount it directly in the specimen holder with no preparation.

NOTE 2—X-ray diffraction patterns collected for specimens consisting of whole chips will reveal the composition of all paint layers probed by the X-rays. The depth probed will depend upon the wavelength of X-ray used, the composition of the paint layer or layers through which the X-rays pass, the composition of the deepest layer probed, the two-theta angle, and other factors. When a copper X-ray tube is used, the depth probed may range from as little as approximately 2 mils (75 μm) in the case of very high density coatings to as much as 197 mils (0.5 cm) in the case of unpigmented resin.

7.1.3 *Paint Film on Panel*—Cut from the panel a specimen of dimensions suitable for mounting in the specimen holder. As an alternative, it may be convenient to cut a piece of specimen to the same dimensions as the specimen holder and use the specimen without the holder.

NOTE 3—An X-ray diffraction pattern collected for coating on a panel will be a superposition of the diffraction patterns of the crystalline components in the coating on the panel and, to the extent that X-rays diffracted from the substrate reach the detector, the diffraction pattern of the substrate.

7.2 Mount the specimen in the specimen holder, taking care to insure that the surface of the specimen is flush with the optical plane of the holder.

NOTE 4—Failure to place the specimen surface in the optical plane illuminated by the X-ray source and viewed by the detector will result in a systematic shift from the correct position of peaks in the observed diffractogram. The greater the shift, the greater the difficulty in using the observed diffractogram to identify components in the specimen.

8. Procedure

8.1 Experimental:

8.1.1 Turn on the diffractometer and allow it to stabilize thoroughly before beginning collection of results. With the aid of the manufacturer’s literature, select instrument operation conditions that permit collection of X-ray diffractograms spanning the two-theta range from 5 to 65°. The conditions chosen must be suitable for qualitative analysis of a multicomponent mixture assuming the presence of a minor component present at approximately one percent by weight. Results collected must be available as the d -spacing and intensity, preferably the integrated intensity, of each peak. In the case of diffractometers not equipped with a computer, the two-theta and intensity data must be measured manually from plotted diffraction patterns and the d -spacings then calculated from the two-theta angles of the peaks. In the latter case, the diffraction patterns must be plotted with two-theta scale expansion that permits the angle of each peak to be measured to the nearest 0.01 Å for peaks in the range above 3.5 Å and to the nearest 0.001 Å for peaks below approximately 3.5 Å.

NOTE 5—If not already established, then make sure that the two-theta calibration of the goniometer of the diffractometer is verified at two or more angles in accordance with recommendations of the manufacturer and corrected as needed. The procedure will entail comparison of the observed and expected d -spacing of diffraction peaks of highly crystalline reference materials at least at one high and one low two-theta angle.

8.1.2 For each sample correct the diffraction pattern spanning at least from 5 to 65° two-theta.

9. Identification

9.1 Prepare a list of all diffraction peaks exhibited by the sample including both the d -spacing and intensity (preferably integrated intensity) of each peak, listed in decreasing order of d -spacing. The d -spacing of each peak should be stated at the nearest hundredth of an angstrom for d -spacings greater than 3.5 Å and stated to the nearest thousandth of an angstrom for d -values of less than about 3.5 Å.

9.2 Identify the crystalline phase or phases that account for all peaks in the diffraction pattern of the sample under analysis, using the Hanawalt Method, Fink Method, or other systematic procedure. Full identification of the crystalline components may be speeded by use of information about components known to be or suspected of being in the sample (that is, preconceived composition) or by use of the list of common pigments and extenders appended (see Table 1).

9.2.1 Verification of Preconceived Components:

9.2.1.1 Prepare a list of components known to be present or suspected of being present on the basis of other information, if any, available to the user. Use the ICDD Alphabetical Index⁷ or other compilation of diffraction peak data to determine the d -values of the three strongest peaks of a suspected component. Compare the three peaks for the suspected component listed in the Alphabetical Index with the set of diffraction peaks observed for the sample under analysis. If any one of the three peaks is absent from the diffraction pattern of the sample, then the suspected component is not present in the sample. (Exception: If a component has one or more peaks with relative intensity much greater than its other peaks and is present at low

⁶ NIST Handbook, X-Ray Recommendations for the International Roentgen Ray Committee on X-Ray Protection, NIST, Gaithersburg, MD, 20899.

⁷ Alphabetical Index—Inorganic Phases, Catalog No. AI42, ICDD.

TABLE 1 Common Pigments and Extenders for Paint

<i>d</i> -Value and Intensity ^A					Name	Formula	ICDD File Number
17.6 _x	9.0 ₅	4.49 ₈	3.58 ₄	1.504 ₆	bentonite ^B	Na _{0.3} (AlMg) ₂ Si ₄ O ₁₀ (OH) ₂ ·H ₂ O	12-219
10.1 _x	4.49 ₉	3.66 ₆	3.36 _x	2.565 ₉	mica ^B	KAl ₂ Si ₃ AlO ₁₀ (OH) ₂	7-25
9.34 _x	4.66 ₉	3.116 _x	2.476 ₇	1.870 ₄	talca ^B	Mg ₃ Si ₄ O ₁₀ (OH) ₂	13-558
7.63 _x	4.283 _x	3.065 ₈	2.873 ₅	2.685 ₄	gypsum	CaSO ₄ ·2H ₂ O	33-311
7.36 _x	4.56 ₅	3.66 ₆	2.451 ₇	1.531 ₇	chrysotile-20rc1	Mg ₃ Si ₂ O ₅ (OH) ₄	25-645
7.31 _x	4.57 ₅	3.65 ₇	2.27 ₃	1.535 ₅	chrysotile-2Mcl	Mg ₃ Si ₂ O ₅ (OH) ₄	31-808
7.17 _x	4.366 ₆	4.186 ₅	3.579 ₈	2.495 ₅	kaolinite ^B	Al ₂ Si ₂ O ₅ (OH) ₄	14-164
4.568 _x	9.12 ₆	4.410 ₂	3.460 ₃	2.853 ₇	zinc phosphate ^B	Zn ₃ (PO ₄) ₂ ·H ₂ O	37-465
4.18 _x	2.69 ₄	2.45 ₅	2.19 ₂	1.72 ₂	yellow iron oxide	FeO(OH)	29-713
4.040 _x	3.136 ₁	2.841 ₁	2.487 ₁	2.486 ₀	crystalalite	SiO ₂	39-1425
3.52 _x	2.370 ₂	1.892 ₄	1.700 ₂	1.667 ₂	anatase	TiO ₂	21-1272
3.445 _x	3.319 ₇	3.103 _x	2.121 ₈	2.106 ₈	barium sulfate	BaSO ₄	24-1035
3.39 _x	6.32 ₂	2.986 ₈	2.840 ₄	2.269 ₂	chrome orange	Pb ₂ (OH) ₂ CrO ₄	8-437
3.38 _x	2.903 ₅	2.787 ₅	2.632 ₃	1.755 ₃	red lead	Pb ₃ O ₄	8-19
3.342 _x	4.257 ₂	2.457 ₈	1.818 ₁	1.542 ₉	quartz	SiO ₂	33-1161
3.310 _x	3.129 ₈	2.926 ₉	1.9103 ₈	1.7642 ₅	zinc sulfide	ZnS	36-1450
3.28 _x	4.96 ₃	4.38 ₃	3.48 ₆	3.03 ₇	lead chromate	PbCrO ₄	8-209
3.260 _x	9.79 ₆	5.771 ₂	4.251 ₂	3.130 ₅	lead oxide sulfate hydrate	Pb ₄ O ₃ SO ₄ ·H ₂ O	29-781
3.260 _x	3.452 ₈	3.006 ₈	2.543 ₆	2.308 ₅	strontium chromate	SrCrO ₄	15-356
3.247 _x	2.487 ₅	2.188 ₃	1.687 ₆	1.624 ₂	rutile	TiO ₂	21-1276
3.22 _x	4.89 ₃	4.72 ₃	3.12 _x	2.668 ₂	moly orange	Pb(Cr ₁₉ Mo ₁₁)O ₄	19-685
3.160 _x	3.583 ₈	3.367 ₆	2.068 ₆	1.761 ₅	cadmium yellow	CdS	6-314
3.142 _x	4.571 ₂	3.494 ₃	3.174 ₂	3.118 ₈	antimony oxide	Sb ₂ O ₃	11-689
3.030 _x	3.852 ₃	2.284 ₂	2.094 ₃	1.8726 ₃	calcite	CaCO ₃	24-27
2.886 _x	2.192 ₃	2.015 ₂	1.804 ₂	1.786 ₃	dolomite	CaMg(CO ₃) ₂	11-78
2.700 _x	3.684 ₃	2.519 ₇	1.8406 ₄	1.6941 ₅	red iron oxide	Fe ₂ O ₃	33-664
2.666 _x	3.633 ₈	2.480 _x	2.176 ₄	1.672 ₉	chrome oxide green	Cr ₂ O ₃	6-504
2.623 _x	4.47 ₆	4.25 ₆	3.61 ₉	3.29 ₉	lead carbonate hydroxide	Pb ₃ (CO ₃) ₂ (OH) ₂	13-131
2.609 _x	7.02 ₉	3.31 ₉	3.08 ₉	2.896 ₇	zinc yellow	K ₂ Zn ₄ (CrO ₄) ₂ ·3H ₂ O	8-202
2.5503 _x	2.8766 ₃	2.3846 ₇	1.6361 ₄	1.4376 ₄	copper chromium oxide	CuCr ₂ O ₄	34-424
2.543 _x	2.984 ₄	2.109 ₂	1.624 ₃	1.491 ₄	tan iron oxide	ZnFe ₂ O ₄	22-1012
2.532 _x	2.967 ₃	2.0993 ₂	1.6158 ₃	1.4845 ₄	black iron oxide	Fe ₃ O ₄	19-629
2.476 _x	2.814 ₆	2.603 ₄	1.625 ₃	1.477 ₃	zinc oxide	ZnO	36-1451
2.443 _x	2.864 ₇	2.026 ₂	1.5602 ₄	1.424 ₄	cobalt aluminum oxide	CoAl ₂ O ₄	10-458
2.338 _x	2.024 ₅	1.431 ₂	1.221 ₂	0.9289 ₁	aluminum metal ^B	Al	4-787
2.091 _x	2.473 ₅	2.308 ₄	1.687 ₃	1.342 ₃	zinc metal ^B	Zn	4-831

^A Subscripts represent the relative intensity (rounded to the nearest integer) of the diffraction peaks of a phase, with the most intense peak taken as 10 and represented by "X."

^B Particles of this material frequently exhibit preferred orientation in paint films, thus causing the observed relative intensities to differ significantly from intensities listed in this table.

concentration, then it may not be possible to observe its weaker peaks.) If all three peaks are present, then make sure that the file number beside the listed *d*-values is noted and the full set of diffraction data for the suspected component is inspected in the Powder Data File.⁵

9.2.1.2 Confirmation of the presence of the suspected component requires that all peaks listed for the suspect in the Powder Diffraction File, or other reference source, must be present in the diffraction pattern of the sample. Furthermore, the relative intensity of the peaks in the diffraction pattern must be similar to the relative intensity of the peaks in the reference pattern when experimental error and possible overlap by peaks of other components are taken into account. Once a component in the sample is identified, make sure that the corresponding set of peaks is either labeled or crossed off the list of peak observed for the sample. However, a peak may be left on the list for further consideration if the observed intensity significantly exceeds the intensity cited in the reference file, thus suggesting that a peak of another component overlaps the one in question. Repeat the procedure stated in 9.2.1 until all preconceived components are confirmed or rejected. Unassigned peaks, if any, remaining on the list prepared in 9.1

represent unidentified components in the sample. Identify these components using one or more of the following methods:

NOTE 6—When comparing the *d*-values of observed peaks with *d*-values of peaks listed in references, allow for reasonable experimental error. As a general rule allow for a margin of error of $\pm 0.02 \text{ \AA}$ for peaks with *d*-values greater than 3.5 Å and $\pm 0.005 \text{ \AA}$ for peaks with *d*-values less than about 3.5 Å. The set of relative intensities observed for the sample under analysis may differ from the values listed in the reference pattern, even when the phase has been correctly identified, because of differences in mode of measurement (that is, peak height instead of peak area), departure of the detector response from linearity, differences in instrument operating conditions, and preferred orientation of pigment particles in the specimen. The effects of preferred orientation are most pronounced for platelet or needle-shaped particles. In the case of mica, with its platelet-shaped particles, the relative intensity of peaks may be changed by a factor of two compared to the reference values.

9.2.2 List of Common Pigments and Extenders (Table 1): Select from the list of observed peaks prepared in accordance with 9.1 the most intense peak or, if some of the peaks have already been identified by use of 9.2.1, the most intense peak that has not been identified. Note the *d*-spacing of the peak and search the first column on the left side of Table 1 to see if the peak is listed. (Allow for experimental error in

accordance with Note 6.) If an apparent match is found, then determine whether the four other d -values listed in the row to the right of the first column are also present in the d -value list for the sample. If any one of the peaks in the row was not observed in the test sample and the listed relative intensity suggests that it should be observable, then the corresponding material is ruled out as a component of the test sample. If all five d -values listed in the row correspond to d -values observed for the test sample, then the material listed in Table 1 beside the row should be given closer scrutiny as a possible component of the sample under analysis. For confirmation, note the ICDD number listed in the column on the extreme right and look up the full diffraction pattern data in the ICDD Powder Diffraction File. Confirmation of the presence of the suspected component requires that all peaks listed for the suspect in the powder diffraction file be present in the diffractogram of the sample. Furthermore, the relative intensity of the peaks of the suspected component in the diffractogram of the test sample must be similar to the relative intensity of the peaks in the reference pattern when the factors stated in Note 6 and possible overlap by peaks of other components are taken into account. When a component in the sample is identified, make sure that the corresponding set of peaks is either labeled or crossed off the list of peaks observed for the sample. Peaks of an identified component that are suspected of overlapping peaks of an unidentified component may be marked as such and retained on the list for further consideration. Repeat the procedure given in 9.2.2 with the most intense unidentified peak or the diffraction pattern until all components in the specimen have been identified or until it has been determined that no unidentified phases in the sample are present on the common component list. Then use the Fink or Hanawalt method, or other systematic system, to identify any remaining unidentified crystalline component.

9.2.3 Hanawalt search: Prepare a list of all peaks in the diffraction pattern of the sample being analyzed, with the peaks listed in decreasing order of intensity. List the intensity of each peak beside the d -value. If two or more peaks have similar intensity and there is uncertainty about which one is more intense, then list the peaks of similar intensity in decreasing order of d -value. If some of the peaks in the diffraction pattern have already been fully accounted for as arising from components known to be present in the sample on the basis of identification using prior knowledge (9.2.1) or the common components list (9.2.2), then these peaks may be omitted from the list. The user then employs the Hanawalt Method and Hanawalt Search Manual to identify the crystalline components that account for the observed diffraction peaks.³

NOTE 7—The Hanawalt Search Manual provides detailed instructions and examples of how to use the Hanawalt Method.

9.2.4 Fink search: Prepare a list of all peaks in the diffraction pattern of the sample being analyzed, with the peaks listed in decreasing order of d -value. List the intensity of each peak beside the d -value. If some of the peaks in the diffraction pattern have already been fully accounted for as arising from components known to be present in the sample on the basis of identification using prior knowledge (9.2.1) or the common components list (9.2.2), then these peaks may be omitted from the list. The user then employs the Fink Search Manual to identify the crystalline components that account for the observed diffraction peaks.⁴

NOTE 8—The Fink Search Manual provides detailed instructions and examples of how to use the Fink Method.

9.2.5 Verification: Prepare a list of all crystalline pigments and extenders identified in the sample, with the components listed in decreasing order of intensity of the most intense peak of each in the diffraction pattern. Examine the list to determine whether it is compatible with other available information about the sample, such as color, elemental content, or chemical composition. Make sure that the user is aware that noncrystalline pigments and extenders are not detected by this method. Infrared spectroscopic analysis, especially when done with a spectrophotometer that spans the region from 4000 to 200 cm^{-1} , and elemental analysis by means of spark emission or X-ray fluorescence spectroscopy are useful supplements to analysis by X-ray diffraction. These spectroscopic techniques are useful to corroborate the presence of crystalline pigments and to indicate the presence of noncrystalline pigments. Resolve any conflict between the list of crystalline pigments and extenders and the other information by repeating the search procedure.

10. Report

10.1 Report the following information:

10.1.1 List all crystalline pigments and extenders in decreasing order of intensity of the most intense peak contributed by each component to the observed diffraction pattern.

11. Precision and Bias

11.1 No numerical statement of precision and bias can be determined in this qualitative test method.

12. Keywords

12.1 crystal; crystalline pigment; extenders; grind paste; grind resin; X-ray diffraction

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