

Microstructure of Aluminum Hydroxides and the Formation of Aluminum Dye Lakes

LYNDON L-S. WOU* and B. A. MULLEY*

Received May 11, 1983, from the *Postgraduate School of Studies in Pharmacy, University of Bradford, Bradford, BD7 1DP, United Kingdom*. Accepted for publication February 22, 1984. *Present address: Beecham Pharmaceuticals Research Division, Animal Health Research Centre, Walton Oaks, Dorking Road, Tadworth, Surrey, KT20 7NT, United Kingdom.

Abstract □ The effect of processing variables on the type of aluminum hydroxide and the dye content of the resultant lakes were investigated. The solid-state structure of aluminum lakes in conjunction with the associated aluminum hydroxide was studied by electron microscopy, X-ray diffraction, and IR spectroscopy. The conditions under which the aluminum hydroxide was prepared were shown to govern the amorphous/crystalline character of the product, which was reflected in changes in particle size and surface area. A hypothesis for the interaction of the dye and aluminum hydroxide is formulated in which the amount of dye adsorbed on the aluminum hydroxide is dependent on the surface area of the microstructures present.

Keyphrases □ Aluminum hydroxides—dye lake formation □ Dye lakes—aluminum hydroxide, processing variables

FD & C aluminum lakes are widely used in edible pharmaceutical inks and to color pharmaceutical tablets, but little has been published about their nature and coloring properties. The conditions of preparation of the aluminum hydroxide, which is the substrate on which the dye is adsorbed to form the lake, have a profound effect on lake formation. The degree of alkalinity, temperature, concentration of reagents, as well as the salts used are all factors affecting the type of aluminum hydroxide formed.

The purpose of this study was to demonstrate that aluminum hydroxide, produced by methods described in lake formation processes, has properties which can be related to products described in the literature outside the laking field. The lake forming qualities of aluminum hydroxides are then evaluated in the context of the extensive fundamental work on the nature of this complex and variable material, which changes so markedly with relatively minor variations in the preparative process.

EXPERIMENTAL SECTION

Materials—Commercial FD & C dyes¹ were used in the preparation of the lakes: FD & C Blue No. 2 dye (lot No. 27390) for lake preparation No. B2; FD & C Red No. 40 dye (lot No. AA7490) for lake preparation No. R40; FD & C Yellow No. 5 dye (lot No. Z9313) for lake preparation Nos. Y5 and 1–21. Commercial lakes¹ obtained for this study were FD & C Yellow No. 5 lake (lot No. 127) and FD & C Yellow No. 6 lake (lot No. 634). Commercial aluminum hydroxides² were obtained as standard samples of different hydrated forms of alumina: gibbsite (lot No. RD 58/78), bayerite (lot No. RD 57/78), boehmite (lot No. RD 59/78), and pseudoboehmite (lot No. RD 60/78). All other reagents were of Analar or laboratory reagent quality.

Standard Procedures—*Preparation of Aluminum Hydroxide (Preparation No. 1)*—This method was based on the Colorcon process, which is comparable with that of Harrison (1). Sodium carbonate solution (0.96 M, 1800 mL) was added in a dropwise manner at 25°C to aqueous aluminum sulfate solution (0.16 M, 1600 mL) at 10–12 mL/min with continuous vigorous stirring. At pH 6.9, addition was halted. The precipitate was stirred slowly for 30 min and kept at pH 6.9 by adding sodium carbonate solution as necessary. The precipitate was washed until sulfate-free (barium chloride test).

Preparation of FD & C Yellow No. 5 Lake (Preparation No. Y5)—FD & C Yellow No. 5 (71 g) was dissolved in distilled water (1400 mL) at 35°C.

The dye solution was passed through a filter into the aluminum hydroxide slurry (prepared in the above process) and stirred for 15 min at 20–25°C. Aluminum chloride solution (5.25 M, 69 mL) was added to the slurry at a rate not exceeding 1 g/min; the final pH was 3.8–4.0. The slurry was stirred slowly overnight. The following morning a few drops of suspended lake were spotted on filter paper to test for bleeding of the dye from the lake. The lake was washed until a 10-mL sample of wash water was no more turbid than the original water by the silver nitrate test. The lake (yield 140 g) was air dried in an oven at 50°C overnight.

Preparation of FD & C Blue No. 2 Lake (Preparation No. B2)—The method was the same as for Yellow No. 5 lake except that FD & C Blue No. 2 (70 g) was dissolved in distilled water (4700 mL) at 55°C. The dye solution was passed through a filter into the slurry and stirred for 15 min at 45–50°C. Aluminum chloride solution (5.25 M, 69 mL) was rapidly added to the slurry; the pH at the end was 4.0–4.1. The yield was 152 g.

Preparation of FD & C Red No. 40 Lake (Preparation No. R40)—The method is the same as for Yellow No. 5 lake except that FD & C Red No. 40 (86 g) was dissolved in distilled water (1400 mL) at 35°C. The yield was 150 g.

Preparation of Aluminum Hydroxide Under Different Conditions—Variations in the processing parameters during aluminum hydroxide precipitation were made by altering the following factors: pH, temperature, aging time, concentration of reagents, presence of sulfate, and nature of aluminum salts and bases. FD & C Yellow No. 5 was the dye used for lake formation in these experiments.

Preparations From Aluminum Sulfate—Since aluminum sulfate is the salt normally used for preparing the aluminum hydroxide substrate for lake formation, this was taken as a starting point for variations in processing parameters to be made. For preparation Nos. 1–4, sodium carbonate solution (1 M or 2 M) was added in a dropwise manner (10 mL/min) into aluminum sulfate solution (0.2 M) varying pH, temperature, and aging time (Table I). Lakes were formed in each case from the sulfate-free precipitate by the standard procedure. For preparation Nos. 5 and 6, sodium carbonate solution (2 M) was added to the aluminum sulfate solution (0.33 M) at 5.5 mL/min until the pH was 10.8, with a large excess of base added to preparation 5. Lakes were formed from the sulfate-free precipitate. By using sodium hydroxide solution (2 M) as the base in preparation 7, the pH of the resulting precipitate was taken up to 12.3. The standard procedure for the preparation of aluminum hydroxide was followed for preparations 9 and 10 except that the sulfate was not removed before lake formation (No. 9) and the precipitation stopped at pH 4.5 (No. 10). For preparations 11–13, sodium carbonate (1 M) and/or sodium hydrogen carbonate solutions (1 M) were added in a dropwise manner into an aluminum sulfate solution (0.2 M) at 10 mL/min until pH 6.9 was reached (Table I).

Preparations From Aluminum Chloride and Nitrate (Nos. 14–20)—Sodium hydroxide (2 M or 4 M) or sodium carbonate solution (2 M) was added to the aluminum chloride solution (0.67 M or 0.5 M) or aluminum nitrate solution (0.67 M or 0.2 M) at 10 mL/min with pH of precipitation and aging conditions given in Table I.

Preparation From Commercial Gibbsite (No. 21)—An attempt was made to form lakes from gibbsite using the standard procedure. After the excess dye was washed off, a slightly yellow grainy material was left.

Lake Analysis—Dye Content—Spectrophotometric analysis was used to determine the dye content of the lakes (2). For all lakes, except FD & C Blue No. 2, a sample (200 mg) in distilled water (200 mL) was boiled (3 min) with sodium hydrogen tartrate (3 g). The solution was cooled and diluted suitably for spectrophotometric analysis by scanning the visible spectrum from 400 to 700 nm. A similar process was used for FD & C Blue No. 2, except that more tartrate (6 g) was required.

Moisture—The methods employed were the Karl Fischer method³ (3) and

¹ Colorcon Inc., West Point, Pa.

² Laporte Industries Ltd., Widnes, Cheshire, United Kingdom.

³ Baird and Tatlock Manual Apparatus; Chadwell Heath, Essex, United Kingdom.

Table I—Effect of Preparation on Type of Aluminum Hydroxide and Lake Obtained (FD & C Yellow No. 5)

Preparation	Concentration, M		Temp., °C	pH	Aging	Aluminum Hydroxide	Dye in Lake, %	Moisture, %		Hardness ^a
	Aluminum Salt	Base						Karl Fischer	Dried at 135°C	
1	Aluminum sulfate 0.2	Sodium carbonate 1.0	20	9	14 d, 20°C	Amorphous	35.6	17.7	19.0	2
2	0.2	1.0	20	7.4	2 h, 70°C	Amorphous, Pseudo-boehmite	29.2	17.0	17.8	6
3	0.2	1.0	20	10	14 d, 20°C	Bayerite, <30% Boehmite	34.1	12.5	15.6	6
4	0.2	2.0	60	10	7 d, 60°C; 21 d, 20°C	Boehmite	39.9	15.9	15.1	2
5	0.33	2.0	20	10.8	21 d, 20°C	Amorphous, Boehmite (poorly crystallized Gibbsite)	36.3	15.6	21.1	9
		(large excess)								
6	0.33	2.0	20	10.8	21 d, 20°C	Boehmite	51.1	6.9	14.6	9
7	0.33	Sodium hydroxide 2.0	20	12.3	21 d, 20°C	Bayerite	7.7	3.5	2.5	1p
9	0.2	Sodium carbonate 1.0	20	6.9	No sulfate washing	Amorphous	21.5	6.9	10.9	2
10	0.2	1.0	20	4.5		Amorphous	31.9	6.4	11.7	2
11	0.2	Sodium carbonate + Sodium bicarbonate 1.0	20	6.9		Amorphous	39.3	15.7	15.4	2
12	0.2	Sodium bicarbonate 1.0	20	6.9		Amorphous	39.5	13.5	14.5	2
13	0.2	Sodium carbonate 1.0	20	6.9		Amorphous	39.3	11.2	12.3	2
14	Aluminum nitrate 0.67	2.0	20	10.5	21 d, 20°C	Boehmite	38.1	10.8	16.4	9
15	0.67	Sodium hydroxide 2.0	20	12.3	3 months, 20°C	Gibbsite	22.6	5.9	5.1	1p
17	0.2	2.0	60	12.2	33 d	Boehmite, (Bayerite,) (Gibbsite)	4.8	3.7	3.1	1p
18	Aluminum chloride 0.67	Sodium carbonate 2.0	20	10.8	19 d, 20°C	Boehmite, (Bayerite)	47.2	14.3	17.8	9
19	0.67	Sodium hydroxide 2.0	20	12.3	3 months 20°C	Gibbsite	7.9	3.0	2.7	1p
20	0.5	Sodium hydroxide 4.0	60	11.8	35 d, 20°C	Gibbsite (plates) Gibbsite + Bayerite (powder)	20.4 14.4	4.4 8.2	4.8 5.4	1p 1p
21	Seeding from sodium aluminate solution (Laporte)					Gibbsite crystals	0.004	~0.7	0.2	g

^a Hardness, an arbitrary scale where 0 is very soft, 9 is extremely hard, g is granular (like sand), and p is powdery.

weight loss on drying, in which samples (0.5 g) were dried to constant weight in a hot air oven at 10°C intervals, up to 135°C (4).

Chloride—The procedure was adapted from a potentiometric titration method (5). The lake sample was dissolved in nitric acid prior to titration against silver nitrate.

Sulfate—A gravimetric method (6) was used. The lake sample was boiled with sodium hydrogen tartrate to form a solution before the addition of barium chloride solution. Chloride and sulfate analyses were done only on the standard lakes.

Physical Investigation of Lakes—Scanning Electron Microscopy⁴—Specimens were mounted on aluminum stubs and gold coated.

Transmission Electron Microscopy⁵—Specimens were prepared by dispersing (1 min) powdered samples in methanol using an ultrasonic bath. A drop of the dispersion was put on a copper specimen support grid which had previously been coated with a thin carbon film.

Infrared Spectroscopy⁶—Pressed disks of potassium bromide (150 mg) containing finely ground sample (1 mg) were used to record the IR spectra.

X-ray Diffraction—The X-ray powder diffraction patterns were taken on an automated diffractometer⁷ equipped with a scintillation detector and pulse-amplitude discrimination, using monochromatic CuK_α radiation.

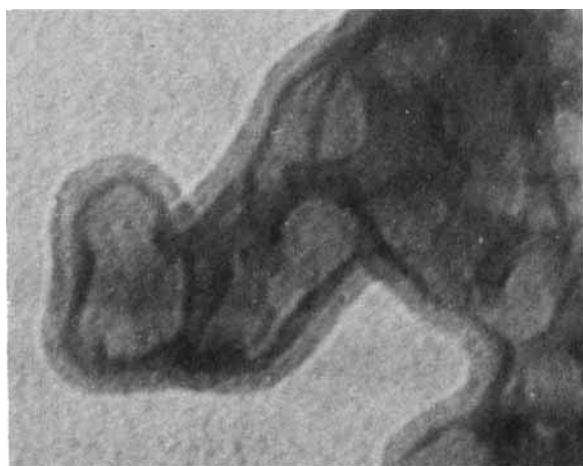
Nitrogen Gas Adsorption—Two methods were used for the determination

⁴ Cambridge Stereoscan 150; Cambridge Instrument Co., United Kingdom.

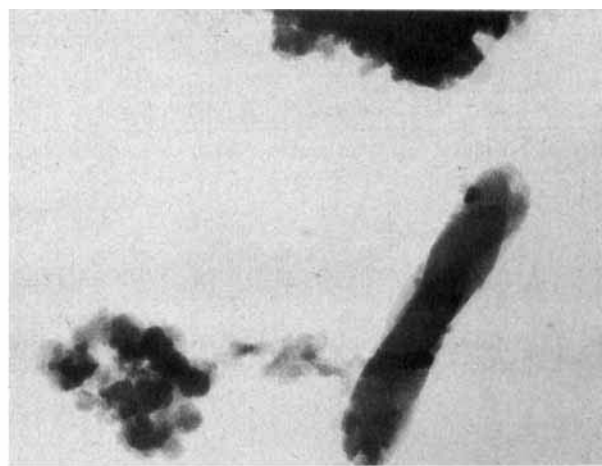
⁵ EMMA-4 Electron Microscope; AEI Scientific Apparatus Ltd., Manchester, United Kingdom.

⁶ Unicam SP 1000 Infra-red Spectrophotometer; Pye Unicam Ltd., Cambridge, United Kingdom.

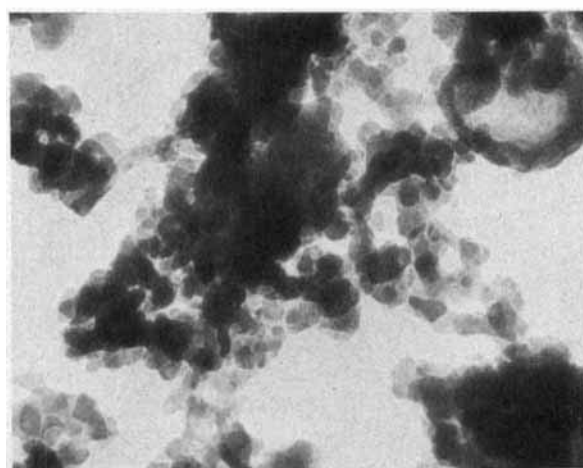
⁷ Siemens AG Kristalloflex 4 Diffractometer; Karlsruhe, West Germany.



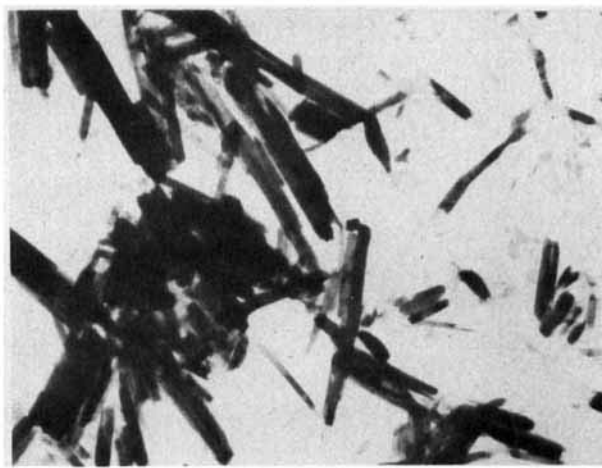
A 20nm



B 0.2μm



C 0.2μm



D 2μm

Figure 1—Transmission electron photomicrographs of precipitated aluminum hydroxide (A), FD & C Blue No. 2 lake (B), FD & C Yellow No. 5 lake (C), and FD & C Blue No. 2 dye (D).

of the surface area of lakes: the static method⁸ using a high-vacuum system and the dynamic method⁹.

RESULTS

Aluminum Hydroxide Substrate—Electron microscopy clarifies the morphology of amorphous precipitated aluminum hydroxide, which was freshly prepared (preparation No. 1). With transmission electron microscopy, the agglomerated particulate material, visible at lower magnifications, are composed of 0.1–0.2- μm diameter aggregated entities, which are primary particles of 10 nm \times 20–30 nm. Each primary particle is composed of finer units, spherules of 2.5–5-nm diameter and possibly even smaller (as shown in Fig. 1A). The precipitate is thus composed of extremely fine particles (spherules) which are fairly homogeneous. This evidence, by transmission electron microscopy, is a considerable help in dispelling speculation on the structure of the gel. Electron diffraction gave a diffuse halo indicating an amorphous material. With scanning electron microscopy (photographs not shown), the precipitate appears as agglomerated material ($\sim 1.6 \mu\text{m}$), apparently composed of 0.15- μm particles; also present is particulate material ($\sim 60 \text{ nm}$). When the same precipitate was dispersed for 85 h on a paint conditioner¹⁰ in an ethanolic shellac solution, the specimen gave the appearance of 0.3–0.7 μm clusters; the smaller clusters seemed to be composed of spherical particles (40–80 nm) in groups.

The morphology of the various known samples of aluminum hydroxides showed the following features in increasing order of crystallinity as indicated from the diffractograms. Pseudoboehmite (RD 60/78) appears as a more compact gel with a more definite form than amorphous aluminum hydroxide (preparation No. 1). Boehmite (RD 59/78) contains more agglomerated material than pseudoboehmite. Bayerite (57/78) consists of a more organized and substantial material with a more definite outline. Gibbsite (RD 58/78) has a crystalline morphology.

IR spectra were obtained for amorphous aluminum hydroxide, pseudoboehmite, boehmite, bayerite, gibbsite, and aluminum hydroxides Nos. 1–20. Good agreement between the spectra for the nonamorphous hydroxides and literature data (7) was observed. Amorphous aluminum hydroxide (Fig. 2) was almost featureless and many of the aluminum hydroxides (Nos. 1–20) were virtually identical. Others were crystalline forms or these mixed with the amorphous variety, and could be identified from the spectra (*e.g.*, gibbsite has strong bands at 3550, 3490, 1020 cm^{-1} ; bayerite at 3580, 3450, 765 cm^{-1} ; boehmite at 3320, 3100, 1080 cm^{-1}). Selected spectra in Fig. 2 show a standard prepared amorphous form, a standard boehmite and No. 4, a standard bayerite, and No. 7, and a standard gibbsite and No. 19.

X-ray powder diffraction patterns (Fig. 3) were obtained for the preparations and complement the IR spectra. Amorphous aluminum hydroxide was devoid of lines, while the crystalline forms had the lines at the appropriate angles from which the d-spacings could be related to literature data (8). Figure 3 shows a prepared amorphous form, a standard boehmite and No. 4, a standard bayerite and No. 7, and a standard gibbsite and No. 19.

Aluminum Lakes—Chemical analyses for the standard lakes are tabulated in Table II for dye, sulfate, chloride, and moisture content with an indication of hardness (on an arbitrary scale, in which 0 represents a very soft lake and 10 is a very hard lake). For the FD & C Yellow No. 5 lakes made under dif-

⁸ Orr Surface Area Pore-Volume Analyzer Model 2100; Micromeritics Instrument Corp., Coulter Electronics Ltd., Dunstable, United Kingdom.

⁹ Quantasorb Surface Area Analyzer; Quantachrome Corp., Greenvale, N.Y.

¹⁰ Red Devil Inc., Union, N.J.

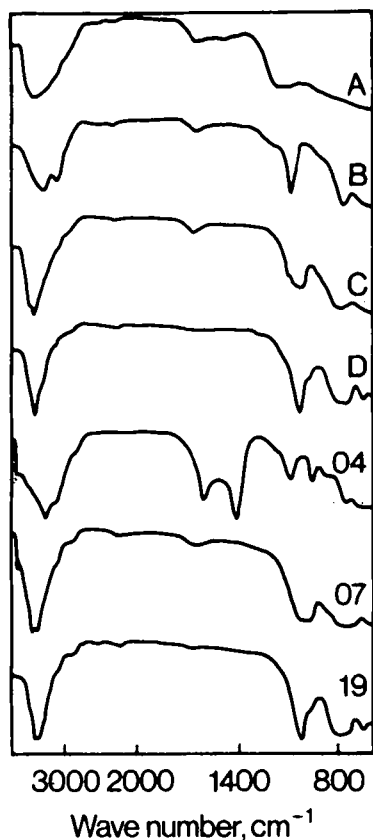


Figure 2—IR spectra standard of aluminum hydroxides. Key: (A) amorphous; (B) boehmite; (C) bayerite; (D) gibbsite and experimental preparations (Nos. 4, 7, and 19).

ferent experimental conditions, the dye and moisture contents with an indication of hardness are shown in Table I. The importance of washing off the sulfate from the aluminum hydroxide substrate is apparent from lake preparation No. 9. The sulfate must compete with dye anions and reduce the dye content of the resulting lake. This has been noted by various patent holders (9).

Transmission electron microscopy shows that the morphology of the FD & C aluminum lakes have a definite similarity to the amorphous aluminum hydroxide (preparation No. 1) but with a denser appearance, presumably caused by a tightly packed layer of dye molecules. FD & C Blue No. 2 lake (B2) contains features of homogeneous "hydroxide" particles as well as cigar-shaped particles (Fig. 1B). FD & C Red No. 40 lake (R40) contains features of homogeneous "hydroxide" particles as well as some U- or oval-shaped particles. FD & C Yellow No. 5 lake (Y5) (Fig. 1C) and FD & C Yellow No. 6 lake (lot No. 634) both have the homogeneous "hydroxide" particles, reminiscent of amorphous aluminum hydroxide. Electron diffraction of the above four lakes gave a diffuse halo indicating the presence of amorphous material. FD & C Blue No. 2 dye (Z7390) appeared as cigar-shaped crystals (Fig. 1D). Electron diffraction gave an array of spots indicating a crystalline material.

Energy dispersive analysis gave a semiquantitative analysis of submicrometer features which conventional forms of analyses cannot do (Table III). Elements lighter than sodium were not detected. For the lakes, the "hydroxide"

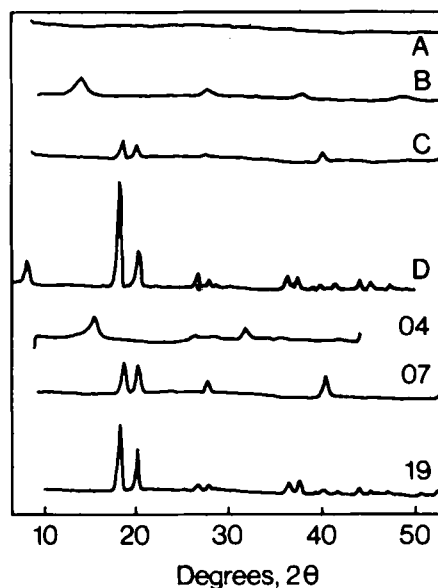


Figure 3—X-ray diffraction pattern of standard aluminum hydroxides. Key: (A) amorphous; (B) boehmite; (C) bayerite; (D) gibbsite, and experimental preparations (Nos. 4, 7, and 19).

particles, which are morphologically similar to the amorphous aluminum hydroxide, have a fairly constant composition. The cigar-shaped particles associated with the Blue No. 2 lake and the U- or oval-shaped particles associated with the Red No. 40 lake have a higher sulfur-to-aluminum content. These particulate materials probably originate from the respective dyestuffs and not from the aluminum hydroxide. The composition of the lakes in terms of the ratio of sulfur to aluminum is in broad agreement with the dye content to aluminum hydroxide ratio (corrected for water content) from bulk chemical analysis.

IR spectra were obtained for FD & C Yellow No. 5 dye and lakes Nos. Y5 (preparations 1-21), FD & C Blue No. 2 dye and lake No. B2, FD & C Red No. 40 dye and lake No. R40, and FD & C Yellow No. 6 dye and lake No. 634. The corresponding lakes of amorphous aluminum hydroxide (Y5), boehmite No. 4, bayerite No. 7, and gibbsite No. 19 are depicted in Fig. 4. The composition of other preparations deduced from the spectra are shown in Table I. The spectra of the lakes show a weakening of the intensity for many of the bands compared with the corresponding dyes, indicating some immobilization of the groups. Frequencies with intensities attenuated after lake formation were found at 1415, 1130, 1040, 1010, 720, 695, and 650 cm^{-1} for FD & C Yellow No. 5 lake (No. Y5). There were also minor band shifts from 1190 and 1220 cm^{-1} to 1140 and 1180 cm^{-1} , respectively. These bands are attributable to sulfonate groups (10). There are, however, no new bands in the IR spectra of the lakes; the spectra are additives of those of the dye and aluminum hydroxide substrate.

All the dyes gave strong X-ray powder diffraction patterns. However, the same dyes "laked" on amorphous aluminum hydroxide gave patterns surprisingly devoid of crystalline structure, having only a "memory" of the derived dye. It was found that the crystal structure of the experimentally prepared lakes closely reflect the crystalline state of the substrate. The diffractograms of the corresponding lakes of amorphous aluminum hydroxide No. Y5, boehmite No. 7, and gibbsite No. 19 are shown in Fig. 5. When the boehmite substrate was "laked" (*i.e.*, exposed to pH 3.8 and dye added) the resulting lakes are essentially amorphous forms such as Nos. 4, 5, 6, 14,

Table II—Chemical Analyses of Standard Lakes

FD & C Dye Lake	Dye, %	Sulfate, %	Chloride, %	Moisture, %		Hardness ^a
				Karl Fischer	Dried at 135°C	
Blue No. 2, (Preparation No. B2)	31.5	5.3	0.17	17.3	17.0	4
Red No. 40 (Preparation No. R40)	45.1	2.7	0.03	14.9	14.4	5
Yellow No. 5 (Preparation No. Y5)	37.6	4.8	< 0.01	12.4	14.7	2
Yellow No. 6 (Lot No. 634)	38.2	5.5	< 0.01	19.2	18.6	1

^a An arbitrary scale: 0 is very soft and 10 is very hard.

Table III—Energy Dispersive Analysis

Sample FD & C Dye	Element	Peak Integral	Relative Proportion ^a	Proportion of atoms
Blue No. 2 dye (Lot No. Z7390)	Na	1225	53.3	31
	S	1102	34.4	20
	Cl	60	1.7	1
Blue No. 2 lake: (Preparation No. B2) 'Hydroxide' particle 'Cigar' particle	Na	292	12.7	1
	Al	1761	65.2	5.1
	S	498	15.6	1.2
	Na	539	23.4	1
	Al	1817	67.3	2.9
	S	1163	36.3	1.6
Red No. 40 dye (Lot No. AA7490)	Na	1078	46.9	4.6
	Si	288	10.3	1
	S	1174	41.9	4.1
	Na	47	2.1	1
Red No. 40 lake: (Preparation No. R40) 'Hydroxide' particle 'U' type particle	Al	1376	51.0	24.3
	S	443	13.8	6.6
	Na	47	2.1	1
	Al	1321	48.9	23.3
	S	529	16.5	7.9
	Na	2204	95.8	75.4
Yellow No. 5 dye: (Lot No. Z9313)	Cl	45	1.3	1
	S	1586	49.6	39
	Al	991	36.7	11.8
Yellow No. 5 lake: (Preparation No. Y5)	Si	87	3.1	1
	S	227	7.1	2.3
	Na	49	2.1	1
	Al	1743	64.6	30.3
Yellow No. 6 lake: (Lot No. 634)	S	695	21.7	10.2
				1

^a Divided by atomic weight.

and 18. Under the acidic conditions of the lake formation process, the boehmitic structure is probably destroyed or modified to an amorphous form of aluminum hydroxide to which the dye is adsorbed. In contrast, the bayerite and gibbsite forms are resistant to phase changes during lake formation. A summary of the effect of preparation method on the type of aluminum hydroxide and the lake obtained is given in Table I.

Gas adsorption results were obtained for the surface areas of aluminum lakes and the substrate of amorphous aluminum hydroxides (Table IV). The Quantasorb gives a favorable comparison with the static method for the specific surface area of a Yellow No. 5 lake (lot No. 127).

DISCUSSION

The conditions of preparation have a profound effect on the type of aluminum hydroxide produced and this in turn influences the dye content and physical properties of the resulting lakes. By means of two complementary techniques, X-ray diffraction and IR spectroscopy, it is possible to decide the type of aluminum hydroxide present.

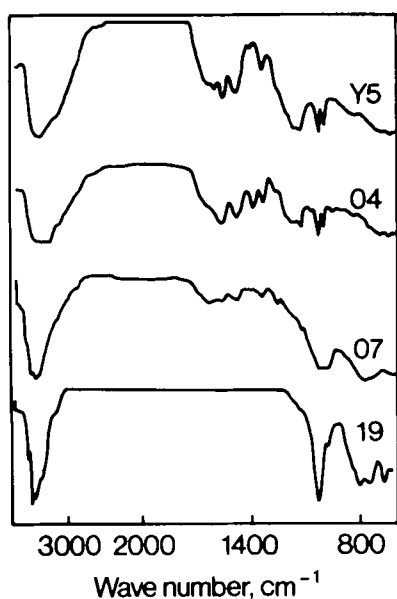


Figure 4—IR spectra of experimentally prepared FD & C Yellow No. 5 dye and lakes Nos. Y5, 4, 7, and 19.

An amorphous aluminum hydroxide gel was produced by the standard method of lake preparation (No. Y5) of aluminum hydroxide from aluminum sulfate and sodium carbonate at pH 6.9. An amorphous product was also obtained from the same reagents at pH 9 with 14 d aging at room temperature (No. 1) and at pH 4.5 (No. 10). When sodium bicarbonate was employed as a base (No. 12) or mixed with sodium carbonate (No. 11) an amorphous gel was prepared. The resulting lakes had a dye content of 36–39% dye (Table I). The preparation (No. 10) with the gel precipitated at pH 4.5 and had a slightly lower dye content of 32%; this may be because some of the aluminum ions were still in solution and the gel was not fully formed. The X-ray patterns for the gel and resultant lakes were featureless.

Petz (11) studied the structure of amorphous aluminum hydroxide gels by radial distribution functions computed from X-ray measurements. He found that the Al³⁺ ion is coordinated by an octahedral arrangement of oxygen sites and the relationship between the remaining oxygens is essentially the same as in water. An "icelike" quasi-lattice was postulated. Recently, Oka *et al.* (12) considered amorphous anodic alumina films to contain AlO₅ coordination polyhedra as well as AlO₄ tetrahedra and AlO₆ octahedra. These polyhedra are envisaged to be arranged in a mixture of two conformations, one of which is a crystalline modification of γ -Al₂O₃ within a short range of radial distance of <0.45 nm and the other is a conformation with randomly arranged coordination polyhedra.

Transmission electron microscopy of amorphous precipitated aluminum hydroxide gel shows "primary" particles of 10 nm × 20–30 nm existing as aggregated entities of 0.1–0.2- μ m diameter, but each "primary" particle is apparently composed of still finer spherules of 2.5–5-nm diameter and possibly

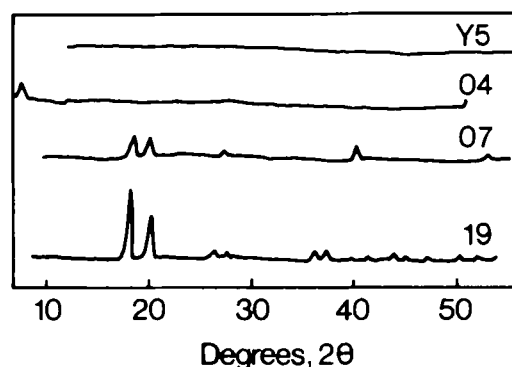


Figure 5—X-ray diffraction patterns of experimentally prepared FD & C Yellow No. 5 dye and lakes Nos. Y5, 4, 7, and 19.

Table IV—Surface Area Measurements of Aluminum Lakes and Their Aluminum Hydroxide Substrate

Sample	Surface Area, m ² /g
	Static Method
FD & C Yellow No. 5 Lake (Lot No. 127)	13.6
	Quantasorb
FD & C Yellow No. 5 Lake (Lot No. 127)	14.1
FD & C Yellow No. 5 Lake (Preparation No. Y5)	33.0
FD & C Yellow No. 6 Lake (Lot No. 634)	27.0
FD & C Blue No. 2 Lake (Preparation No. B2)	27.5
FD & C Red 40 Lake (Preparation No. R40)	18.2
Amorphous Aluminum Hydroxide (Preparation No. 1)	114

even smaller (Fig. 1A). This is in accordance with Lippens and Steggerda (13), who are of the opinion that amorphous material consists of spherical particles 2–5 nm in diameter, loosely aggregated to bigger units.

From the nitrogen adsorption results, the standard lakes have specific surface areas less than one-third of that for the substrate amorphous aluminum hydroxide (Table IV). This may be interpreted as follows: the adsorbed layer of dye molecules on the surface of the aluminum hydroxide envelopes the micropores (pores with radii ~ 1.5 nm) and probably some of the mesopores (intermediate pores with radii of 1.5–100 nm). Thus, in the lakes, nitrogen can only be adsorbed on the dye-enveloped aluminum hydroxide, which is "smoother" since the larger dye molecules are either blanketing the micropores so that there are fewer sites for adsorption or else steric hindrance repels the nitrogen molecules, resulting in a considerable reduction in the measured specific surface area.

X-ray diffraction of the FD & C dyes, *i.e.*, Blue No. 2, Red No. 40, and Yellow Nos. 5 and 6, all show a large number of sharp lines, indicating the dyes are highly crystalline. However, lake formation of the same dyes with amorphous aluminum hydroxide gives a rather diffuse X-ray pattern in the region of the sharp lines of the dyes. The lakes are thus amorphous. Electron diffraction, associated with transmission electron microscopy, also gives the same results. Electron diffraction enables small, identifiable regions of a few cubic micrometers to be examined, whereas X-ray diffraction needs several cubic millimeters of sample, although the information obtained by the latter is more accurate.

Kiel and Heertjes (14) found that the calcium–aluminum lake of alizarin shows four sharp lines on a powder X-ray diagram indicating that the substance is highly crystalline. Furthermore, its IR spectra had some new bands, which the alizarin did not exhibit.

The IR spectra of the FD & C dyes have a number of peaks of strong intensity while the corresponding lakes have attenuated absorption bands. Since the bands attributed to sulfonate groups are immobilized, the IR spectra indicate that in all the lakes used, the sulfonate group is involved in bonding the dye to the aluminum hydroxide. This conclusion is in agreement with Cummings *et al.* (15), who suggested that the adsorbed dye anions forming the monolayer could be composed of monodispersed anions, each orientated with all the sulfonate groups as close as possible to the surface. The adsorption mechanism is probably an exchange of chloride ions for the adsorbed anions, but there may also be some covalent bonding occurring. In the laking process, pretreatment of the substrate with an acid covers the surface with anions that may be either covalently bound or present as ions. The anion may be replaced by dye anion, and it is this reaction that is the basis of the alumina dyeing process (16, 17). Under the laking conditions (pH 3.8–4.0) the aluminum hydroxide particles are positively charged enabling interaction to take place with anionic dyes. The importance of the surface charge on aluminum hydroxide particles and its dependence on pH has been recently studied (18–21).

Boehmite was produced from aluminum sulfate and sodium carbonate under alkaline conditions, but the condition of pH 7.4 for 2 h at 70°C produced pseudoboehmite, which was boehmite in an excess of amorphous gel (No. 2). Preparations at pH 10 and aging under various conditions also produced boehmite (Nos. 3, 4, 5, and 6). Aluminum nitrate and aluminum chloride, precipitated with sodium carbonate under alkaline conditions (pH 10), also produced a boehmitic gel (Nos. 14 and 18, respectively). Some of the boehmites produced lakes with a higher dye content than with the amorphous gels, *e.g.*, No. 6 contains 51% and No. 18 47% dye content but these were both very hard (Table I).

There is controversy in the literature concerning the mechanism by which aluminum hydroxide gels change during the aging process. The term "aging" is used to connote all irreversible structural or textural changes in the colloidal system which may occur after flocculation or gelation (22). Aging is a complex phenomenon. Water plays a key role in all the aging mechanisms. The poorly organized flocculated hydroxide prepared from salts of hydrated cations

usually contains large quantities of molecular water (22). Baker and Pearson (23) propose that it is not a large conceptual step from the hydrolytic polymers in aluminum salt solutions [the dimer, $\text{Al}_2(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$, for example] to the small boehmite-like crystallites capable of giving an X-ray diffraction pattern. Thus, pseudoboehmite is nothing more than an aggregate of ultra small boehmite-like crystallites, and a boehmitic pattern in crystallites as small as ~ 2.5 nm can be detected. The end point of the hydrolytic polymerization may be either an infinite series of chains (*i.e.*, the boehmitic-like materials) or ring structures (*i.e.*, gibbsite or bayerite).

Serna *et al.* (24) have found that sulfate and carbonate anions both show evidence of coordination with the surface aluminum cations. The carbonate interaction appears to be the strongest and is believed to be responsible for the relatively high degree of stability of carbonate-containing aluminum hydroxide gel. This could explain why the gel from sodium carbonate did not age beyond boehmite at pH 10. Only Baker and Pearson's (23) chain structure could be formed and not the ring structure. It is interesting to see from the X-ray diffraction patterns that the boehmite degenerated to various amorphous forms after lake formation, although IR spectroscopy still detected the boehmite.

On aging of the precipitate at pH ~ 12 , gibbsite is formed from sodium hydroxide with aluminum nitrate (No. 15), and similarly with aluminum chloride (No. 19). However, at 60°C with aging, some less well crystallized material is formed: sodium hydroxide with aluminum nitrate (No. 17) forms gibbsite with bayerite and boehmite, while sodium hydroxide with aluminum chloride (No. 20) forms gibbsite and bayerite. It is noteworthy that the aged product of aluminum sulfate precipitated with sodium hydroxide at pH 12 is in the form of bayerite (No. 7). The reason may be that the sulfate coordinates to the aluminum and inhibits crystallization to the gibbsite phase. The aluminum nitrate and chloride salts, precipitated with sodium hydroxide at pH 12 with aging, both crystallize to the same end product, gibbsite. This is in line with the hypothesis that the rate of aluminum hydroxide crystallization is inversely related to the tendency of anion inclusion in aluminum hydroxide precipitates (25). The precipitation at 60°C to produce a mixed product (gibbsite plus bayerite or boehmite) happens since at elevated temperature there is a "fast" transformation to a boehmitic structure which only slowly, with aging, crystallizes to the trihydroxides.

The lakes containing gibbsite or bayerite have a much lower dye content than the amorphous lakes [lake Nos. 7, 17, and 19 contain 8, 5, and 8%, respectively, while gibbsite crystals (No. 21) adsorb a negligible amount of dye (Table I)]. This may be explained from surface area considerations. Crystalline gibbsite evidently has the least surface area available for adsorption of dye since most of the aluminum atoms are incorporated in the crystal lattice and are unavailable for adsorption. The morphology of gibbsite from transmission electron microscopy consists of straight edges and hexagonal shapes. Lippens (26) prepared gibbsite crystals in the form of hexagonal platelets of diameter 0.3 μm , and rod-shaped crystals $10 \times 3 \mu\text{m}^2$. Hence the surface area was quite small. Bayerite particles range from ~ 50 to 100 nm upwards, forming larger aggregates. Lippens (26) found that the surface area of bayerite was 6–75 m^2/g and his micrographs showed bayerite particles, called somatoids, which had a variable size, with the width being mostly smaller than 0.5 μm with a length 3–10 times the width. In contrast, Lippens and Steggerda (13) found the surface area of gelatinous boehmite to be ~ 200 –500 m^2/g . An amorphous gel of spherical particles of 2–5-nm diameter would be expected to give a surface area of $\sim 1000 \text{ m}^2/\text{g}$, but Lippens and Steggerda (13) were unable to measure the surface area by the nitrogen Brunauer, Emmett, and Teller (BET) method, since it was found that the surface was not accessible to nitrogen.

Recently, Pyman and Posner (27) have questioned the meaning of the term "surface area," since amorphous materials generally have large surface areas of 50–1000 m^2/g , a considerable pore structure which is frequently microporous, and contain appreciable quantities of water, both adsorbed onto the surface and incorporated into the structure. They suggest that assignment of a specific surface area to amorphous materials should be related to the purpose for which the surface is to be used and that the value is dependent on the method. With lakes formed from the amorphous aluminum hydroxide gel, which are believed to be composed of spherules 2.5–5 nm in diameter from the transmission electron microscopy work, the envisaged surface area of 1000 m^2/g may be regarded as an effective surface area from the viewpoint of the dye anions. Such a surface is not accessible to nitrogen adsorption, which gives a lower surface area value of 114 m^2/g $\text{Al}(\text{OH})_3$ (Table IV). It appears that nitrogen envelopes the 10–30 nm particles without being able to reach the spherules of 2.5–5 nm.

From these considerations the following picture of lake formation is proposed. In aluminum lakes, the amount of dye adsorbed on the aluminum hydroxide is dependent on its surface area. The dye molecules are envisaged to form a monolayer on the surface of amorphous aluminum hydroxide spherules of 2.5–5-nm diameter, which provides sufficient surface area to account for

the 30-40% dye content of aluminum lakes. Direct evidence for the existence of these spherules comes from the highest power transmission electron micrographs. This conclusion is supported by the work of Lippens and Steggerda (13) who have also described amorphous aluminum hydroxide gel as being composed of 2-5-nm diameter spherical particles, loosely aggregated to form larger units. Further it agrees with the results of Bye and Chigbo (28) where they found weakly bonded flocs of apparently isometric particles of ~5 nm.

The quantity of dye adsorbed in terms of mmol dye/g Al_2O_3 [notation after de Boer *et al.* (29)] is readily calculated from the lake dye content. Since aluminum hydroxide has a variable water content, the formula $2Al(OH)_3$ may be written as $Al_2O_3 \cdot 3H_2O$, and Al_2O_3 is expressed as that equivalent amount of aluminum hydroxide with no water content. For aluminum lakes, the quantity of dye adsorbed was found to be ~2 mmol/g Al_2O_3 for Blue No. 2 and Yellow No. 5 and ~3 mmol/g Al_2O_3 for Yellow No. 6 and Red No. 40. Giles *et al.* (16) have made studies of dye adsorption on anodic films and found that for disulfonated dyes there was a maximum adsorption of ~0.2 mmol/g corresponding to ~100 m²/g, the adsorbed dye molecule generally being orientated "edge-on." Since aluminum lakes contain about 10 times more dye than the anodic films of Giles, this suggests that the surface area of substrate covered would be in the order of 1000 m²/g and is consistent with the spherule size of 2.5-5-nm diameter. However, the nitrogen gas adsorption results give a surface area of amorphous aluminum hydroxide gel compatible with a "primary" particle size of 10 nm × 20-30 nm. The surface of the 2.5-5-nm diameter spherules is presumably inaccessible to nitrogen and thus the smallest particle penetrable by nitrogen may contain many crystallites. Baker and Pearson (23) suggested that the packing of these crystallites reduces the accessible surface to nitrogen. It may be firmly concluded that the evidence points to the dye being surface adsorbed on very small particles, mainly <50 nm.

These experiments provide good evidence that the fully amorphous type of aluminum hydroxide is the best form for lake formation confirming what is empirically known within the industry. It is also evident that the gel should be washed free of sulfate ion before laking to avoid interference with dye adsorption. The conditions under which the aluminum hydroxide is prepared governs the degree of amorphous/crystalline character of the product, which is reflected in changes in particle size and surface area of the aluminum hydroxide. This then controls the amount of dye taken up. Although lakes can be formed from boehmite, the product is usually hard and glassy; thus the product is unsuitable for industrial use. The crystalline trihydroxides, bayerite and gibbsite, produced under aging conditions, take up considerably less dye. Gibbsite crystals take up a negligible amount of dye. To prevent lake formation failure, aging conditions, which are likely to produce the crystalline forms of aluminum hydroxide, should be avoided.

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