

SCIENTIFIC SECTION

DISCOVERY OF THE ALKALOIDAL AFFINITIES OF HYDROUS ALUMINUM SILICATE.*

BY JOHN URI LLOYD, PHAR.M.

TABLE IV.

(1)	14 Gm. were required to precipitate	1 Gm. quinine bisulphate.
(2)	22 Gm. were required to precipitate	1 Gm. quinine bisulphate.
(3)	50 Gm. were required to precipitate	1 Gm. quinine bisulphate.
(4)	60 Gm. were required to precipitate	1 Gm. quinine bisulphate.
(5)	60 Gm. were required to precipitate	1 Gm. quinine bisulphate.
(6)	70 Gm. were required to precipitate	1 Gm. quinine bisulphate.
(7)	70 Gm. were required to precipitate	1 Gm. quinine bisulphate.
(8)	100 Gm. were required to precipitate	1 Gm. quinine bisulphate.
(9)	100 Gm. were required to precipitate	1 Gm. quinine bisulphate.
(10)	100 Gm. were required to precipitate	1 Gm. quinine bisulphate.
(11)	110 Gm. were required to precipitate	1 Gm. quinine bisulphate.
(12)	120 Gm. were required to precipitate	1 Gm. quinine bisulphate.
(13)	150 Gm. were required to precipitate	1 Gm. quinine bisulphate.
(14)	150 Gm. were required to precipitate	1 Gm. quinine bisulphate.
(15)	150 Gm. were required to precipitate	1 Gm. quinine bisulphate.
(16)	150 Gm. were required to precipitate	1 Gm. quinine bisulphate.
(17)	150 Gm. were required to precipitate	1 Gm. quinine bisulphate.
(18)	204 Gm. were required to precipitate	1 Gm. quinine bisulphate.
(19)	800 Gm. were required to precipitate	1 Gm. quinine bisulphate.
(20)	1000 Gm. were required to precipitate	1 Gm. quinine bisulphate.

To the surprise and disappointment of both Dr. Parsons and myself, the alkaloidal affinities of these various specimens did not parallel their decolorizing qualities, as determined by Dr. Parsons. For example, one specimen that stood very high as a decolorizer was very low as regards alkaloidal affinities. Nor were colloids prepared by me from other sources capable of paralleling each other in adhesion intensity for different alkaloids, as shown in Table V, following.

TABLE V.²⁵

Comparative Energies of Two Specimens of Colloid from Fullers' Earth.

	Amount required.	
	First source.	Second source.
1 Gm. cocaine hydrochlorate	13 Gm.	10 Gm.
1 Gm. strychnine sulphate	11 Gm.	10 Gm.
1 Gm. morphine sulphate	6 Gm.	4 Gm.
1 Gm. brucine sulphate	9 Gm.	6½ Gm.
1 Gm. codeine sulphate	5 Gm.	5 Gm.
1 Gm. quinine bisulphate	15 Gm.	8 Gm.
1 Gm. cinchonine sulphate	10 Gm.	10 Gm.
1 Gm. cinchonidine sulphate	9 Gm.	10 Gm.
1 Gm. atropine sulphate	8 Gm.	8 Gm.

* Continued from p. 390, April issue.

²⁵ Of the whole line of perplexities and possibilities, the most perplexing problem to me is perhaps the evidence of such discordant results as shown in Table V.

Note the remarkable variation in the amount of colloid required to precipitate the *same amount* of a given alkaloid. While in general the reagent obtained from the second source is noticeably more energetic than from the first source, they are alike in energy as regards their reaction with atropine sulphate, codeine sulphate and cinchonine sulphate, while with cinchonidine sulphate the first colloid is more energetic than the second!

What is Fullers' Earth?—Some specimens of "fullers' earth" are of no alkaloidal value whatever, while some that rank well in this respect are naturally so foul and dirty as to forbid the very thought of putting them into the stomach. Dr. Parsons writes as follows:

Though samples of fullers' earth from different parts of any one deposit, or indeed from any one locality, are much alike, samples from different localities are so different in their physical properties that it is by no means easy to classify them. To determine whether or not a particular clay is a fullers' earth is no simple matter, for its bleaching power is practically the only characteristic by which it may be identified. Among the properties formerly attributed to fullers' earth are non-plasticity, disintegrating in water, detergent action, large water content, and the property of adhering to the tongue.

In this Dr. Fantus also agrees, as evidenced by the following, from his most recent article:

The power of adsorbing alkaloids is strongly developed in some fullers' earths, and very feeble in others. The adsorptive value of commercial fullers' earths should be stated by the dealers; and pharmacists should demand specimens of high activity. Lloyd's reagent possesses this power to the highest degree.

Fullers' earth is not synonymous with kaolin, as the United States Dispensatory and the National Dispensatory would lead us to infer. It is a substance with markedly different properties.—*Jour. Amer. Med. Assn.*, May 29, 1915.

Analyses of Fullers' Earth and Related Clays (by Mr. A. F. Price).—During my search for American fullers' earths capable of yielding the active colloids, Dr. John H. Dawson, of the United States Customs Service, San Francisco, introduced me to Mr. A. F. Price, who has had great experience in the analysis of clays and minerals of the West, and whose father (Professor Thomas Price) was celebrated in earth and mineral analyses. Mr. Price entered with enthusiasm into the subject, both because of his hope of developing a new process of clay valuation, and because he had long been professionally confronted with the commercial uncertainties of fullers' earth. He had already decided that the useful substance contained therein must be considered from its physical or colloidal aspect, and that chemical analytical processes were inadequate as standards of commercial valuations. He also described the processes of making from crude clays and clay mixtures the commercial, powdered fullers' earth, as follows:

Treatment of Fullers' Earth.—In this method, even those portions of the strata of fullers' earth which are now commercially valueless can be utilized. The different qualities of fullers' earth are thoroughly mixed, blended and amalgamated by grinding them, with the addition of water, to a slurry. The slurry is run into reservoirs, and allowed to settle. All water rising to the surface is removed and the residue is dried. The product is of uniform strength, quality and color.

Machine for Washing and Refining Fullers' Earth, China Clay, etc.—The fullers' earth is placed in a tank and mixed with water; it then goes to a second tank provided with an agitator to complete the mixing; and then to a refining machine consisting of two stationary concentric cylinders and an inner vessel like an inverted cone, having slots in, and projecting strips on, its sides. By the rotation at about 100 r.p.m. the coarser particles are driven against the walls of the inner cylinder and fall on the bed plate at its base, whence they are swept into the

annular space between the two cylinders by curved radial arms revolving with the inner vessel, and can be removed from time to time. The finer particles remain in the inner vessel, whence they flow into the settling tanks.

Mr. Price supplied me with a number of analyses of fullers' earths, made by his father and himself. These, in the paucity of published analytical reports, I include herewith. But as yet I have had no opportunity of paralleling these assays with an examination for their alkaloidal affinities.

Analyses, by A. F. Price, of Samples of Material Received from The Associated Oil Company.

	February 3, 1911.				
	No. 1. Percent.	No. 2. Percent.	No. 3. Percent.	No. 4. Percent.	No. 5. Percent.
Silica	52.89	55.73	54.25	58.15	54.08
Alumina	23.81	25.33	26.76	24.64	24.07
Ferrous oxide	1.67	1.25	1.34	1.05	1.93
Calcium oxide	2.52	2.06	2.35	1.23	2.15
Magnesium oxide	3.05	3.10	2.41	2.15	2.20
Alkalies	1.04	1.31	1.38	1.18	1.08
Carbon dioxide	0.61	0.55	0.61	0.81	1.05
Water	13.85	10.05	10.25	9.97	12.50
	<hr/> 99.44	<hr/> 99.38	<hr/> 99.55	<hr/> 99.18	<hr/> 99.06
	No. 6. Percent.	No. 7. Percent.	No. 8. Percent.	No. 9. Percent.	No. 10. Percent.
Silica	54.36	54.73	54.35	55.89	57.28
Alumina	26.25	24.18	23.28	23.56	25.42
Ferrous oxide	1.78	1.02	2.12	1.23	2.01
Calcium oxide	1.32	3.61	1.83	2.31	2.26
Magnesium oxide	3.33	1.43	1.38	3.04	3.12
Alkalies	1.03	0.87	1.21	0.83	1.05
Carbon dioxide	0.85	2.83	trace	0.50	0.81
Water	10.55	10.65	15.10	12.10	7.60
	<hr/> 99.47	<hr/> 99.32	<hr/> 99.27	<hr/> 99.46	<hr/> 99.55

List of Analyses of Recognized Fullers' Earth from Well-known Localities, Submitted for Purposes of Comparison with Our Report of This Date to The Associated Oil Company.

February 3, 1911.

Fullers' Earth from South Dakota.

	Percent.	Percent.	Percent.	Percent.	Percent.	Percent.
Silica	68.23	60.16	56.18	55.45	57.00	68.72
Alumina	14.93	10.38	23.23	18.58	17.368	16.90
Ferrous oxide	3.15	14.868	1.26	3.82	2.63	4.00
Calcium oxide	2.93	4.96	5.88	3.40	3.00	4.06
Magnesium oxide	0.875	1.714	3.29	3.50	3.027	2.56
Water	6.20	7.20	11.46	8.80	9.50	8.10

It is claimed that the material from South Dakota is fully equal to English fullers' earth, three analyses of which are given below:

	Percent.	Percent.	Percent.
Silica	44.00	55.48	60.90
Alumina	23.06	19.16	18.34
Ferrous oxide	2.00	11.78	10.00
Calcium oxide	4.17	3.10	2.36
Magnesium oxide	2.00	3.71	1.52
Alkalies	1.72
Water	24.95	6.75	4.89

The following are analyses of fullers' earth from Florida:

	Percent.	Percent.	Percent.
Silica	60.53	55.05	59.02
Alumina	20.13	22.88	11.88
Ferrous oxide	7.47	7.14
Calcium oxide	2.57	4.77	6.48
Magnesium oxide	2.12	0.43	3.24
Water	14.75	10.42	11.13

Standard Analyses of Fullers' Earth and Various Clays.

	Bakersfield Fullers' Earth. Percent.	English Fullers' Earth. Percent.
Silica	54.32	54.20
Alumina	18.88	14.30
Ferric oxide	6.50	6.30
Lime	1.00	1.25
Magnesia	3.22	2.72
Loss on ignition	11.86	17.44
Alkalies (by difference)	4.22	3.79

Kaolin Clays.

	Percent.	Percent.	Percent.
Silica	62.40	46.28	72.30
Alumina	26.51	36.25	18.94
Ferric oxide	1.14	1.64	0.40
Lime	0.57	0.192	0.58
Magnesia	0.01	0.321	0.39
Water	8.80	13.53	7.04

Sewer Pipe Clays.

	Percent.	Percent.	Percent.
Silica	57.10	63.00	59.56
Alumina	21.29	23.57	15.76
Ferric oxide	7.31	1.87	7.72
Lime	0.29	0.46	0.60
Magnesia	1.53	0.89	0.93
Water	7.35	6.45	7.70

Brick Clay.

	Percent.	Percent.	Percent.
Silica	52.30	71.56	42.28
Alumina	18.85	13.86	8.26
Ferric oxide	6.55	4.78	3.84
Lime	3.36	0.50	13.05
Magnesia	4.49	0.11	6.01
Water and carbonic acid	22.07

Analyses of Slip Clays for Glaze.

	Percent.	Percent.	Percent.
Silica	55.40	43.94	63.63
Alumina	14.80	11.17	13.57
Ferric oxide	5.80	3.81	7.77
Lime	5.70	11.64	2.55
Magnesia	2.48	4.17	1.47
Water	5.18	3.90	4.75

Clays for Hollow Bricks and Fireproofing.

	Percent.	Percent.	Percent.
Silica	52.22	57.57	51.90
Alumina	29.45	21.70	18.34
Ferric oxide	2.78	2.26	7.50
Lime	0.88	0.32	4.14
Magnesia	0.72	1.12	3.30
Water	11.10	6.78	7.39

	Pressed Bricks.		Clay for Paving Brick.	
	Percent.	Percent.	Percent.	Percent.
Silica	65.78	68.28	56.00	74.25
Alumina	14.79	18.83	22.50	22.33
Ferric oxide	8.03	2.60	6.70	5.75
Lime	0.54	0.70	1.20	3.42
Magnesia	1.42	0.13	1.40	3.47
Water	4.68	7.81	7.00	1.13

Bentonite Clay.

Used for the manufacture of both ordinary and pressed bricks (and having none of the properties of fullers' earth).²⁶

	Percent.	Percent.	Percent.
Silica	59.78	61.06	63.25
Alumina	15.10	17.12	17.62
Ferric oxide	2.40	3.17	3.70
Lime	0.73	2.69	4.12
Magnesia	4.14	1.82	3.70
Water	16.26

Well-known Fire Clays.

	Silica.	Alumina.	Water.	Balance.
	Percent.	Percent.	Percent.	Percent.
Stourbridge	65.10	22.22	7.10	5.57
	63.50	23.30		10.30
Dowlais	67.12	21.18	4.32	7.38
	58.10	26.59	7.57	7.74
French	63.57	27.45	8.64	0.74
Cornwall	47.75	38.11	12.54	1.30

To these analyses of commercial fullers' earths, I append Dr. Waldbott's analysis of "Lloyd's reagent," with his comments thereon, as follows:

The reagent has approximately the following composition: H₂O, 17.41 percent; SiO₂, 55.30 percent; Al₂O₃, 9.82 percent; Fe₂O₃, 14.18 percent; CaO, 1.58 percent; CO₂, percent not determined. Heating the material to about 130° did not destroy its peculiar activity; but a red heat expelled an additional quantity of water, rendering the reagent inert. When the reagent is exhausted with hydrochloric acid, the residual earth is still effective. The activity of the reagent is not impaired by concentrated nitric acid or by *aqua regia*. After the alkaloid has been removed from its combination with the reagent, the residual material retains the full effect. This process results in a jelly difficult to filter and slow to settle; it is precipitated readily by addition of an acid; or an alkaloidal salt. In drying, the jelly shrinks to a very small bulk; conversely, the solid expands remarkably in contact with water. The jelly precipitates inorganic salts also, *e.g.*, barium chloride, lead acetate, zinc sulphate, etc.²⁷

²⁶ This statement is not correct if it is the bentonite I now know.—A. F. P.

²⁷ Journal of the American Chemical Society, vol. xxxv, No. 6, June, 1913.

The Term "Adsorption."—The nature of the alkaloidal reaction that I have considered under the word "*affinity*" may, I hope, be properly touched by me without intruding on scientific researches now being made by others. I have accepted that, for purposes of expression, this term "*affinity*" may be more restricted, by regarding the phenomenon as one of *adsorption*. I am the more inclined to this view, not only because the phenomenon seems *not* to be governed by atomic valency (see Table V), but because writers have always employed the word "*adhesion*" in connection with the attractive decolorizing action of fullers' earth. The *physical* condition of the material being all-important to the phenomenon points also in that direction. In this I take the liberty of extracting the following from a letter by my friend, Dr. R. G. Eccles, of Brooklyn, New York:

Adsorption is of exceedingly great interest in biology, and is at present commanding a vast amount of attention from physico-chemists. The word *adsorption* combines the two meanings of *adhesion* and *absorption*. The word *adhere* means simply to stick to, as by the use of paste, glue, or atmospheric pressure of a leather sucker to a stone. The word *absorb* applies to the taking up of a solution by blotting paper or a sponge. *Adsorption* does not appear to be either *adhering* or *absorbing*, but more like the taking up of hydrogen by platinum sponge, or like the precipitating and coagulating of colloidal proteins by contact with reacting agents of a chemical kind. It manifests at one and the same time a resemblance to *adhesion* and *absorption*.²⁸

The eminent authority, Dr. Gordin, has used no other expression relating to this phenomenon, to which I may add that Dr. Wolfgang Ostwald,²⁹ of the University of Leipsic, Germany, who in the spring of 1914 spent some time in my laboratory, studying several phases of mutual interest in the direction of capillary and colloidal phenomena that my special line of researches had developed, accepted that view of the reaction. And yet, more than one phase of the subject still proves to me very perplexing. For example, the alkaloid sanguinarine is insoluble and white, but produces *red salts*. A mixture in water, of *white*, ammonia-made Lloyd's reagent, insoluble, alkaline, with *white* sanguinarine (practically insoluble) produces gradually a *red* alkaloidal compound, insoluble in dilute acid water. If this phenomenon be *adhesion*, *purely*, the reagent has the power of reddening this white alkaloid, giving to the *adhesion* product the color of the *salts* of sanguinarine. As a contrary view, may I not call attention to some of the phases of manipulation aforementioned, that seem to show that no exact chemical valency exists (see Table V)?

But I must not intrude further, for all such problems and outreaches are (or will be) in the hands of special investigators. This contribution is intended to introduce only enough chemistry and physics to elucidate the various problems I had to meet, in the face of lack of print or personal knowledge of anyone. The alkaloidal affinities of the substance under consideration seemed to be unknown.

²⁸ From letter of Dr. R. G. Eccles, Brooklyn, N. Y., June 21, 1915.

²⁹ After returning to Germany, Dr. Ostwald obtained from me considerable amounts of this reagent. He instituted systematic researches in the University laboratory, being deeply interested in the subject. Dr. Ostwald is also an officer in the German Army, and is now serving in the trenches.

Editor's Notes.—Last month Professor Lloyd lectured in several Colleges of Pharmacy and demonstrated the action of hydrous aluminum silicate with alkaloids. A series of slides were projected on the screen, showing several of the alkaloids in the magma, in their development from a colloidal condition to crystalline forms.

Related contributions by Professor Lloyd that appeared in the Proceedings of the American Pharmaceutical Association from 1871 to 1885 will be translated (part have been), for publication in the Zeitschrift für Chemie und Industrie der Kolloide.