ON THE ADSORPTION OF ANILINE-BLUE BY SOME PORCELAIN CLAY.

BY

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Some years ago, Ashley concluded that the plasticity of clay depends mostly on the colloids present and is directly proportional to their amount. As adsorption is an essential property of all colloids (gels) and also of plastic clays, we come naturally to the conclusion that the plasticity of a clay can be measured numerically by means of its adsorptive power.

Now, a plastic clay adsorbs various dyestuffs of complex constitution, for instance, aniline-red, aniline-blue, victoria-blue, violet, malachite-green and diamond-green among the anilinedyes; oricine and safranine among the plant dyes and carmine among the animal dyes. Hence we can express the adsorptive power of a clay by the term of the partial loss of colour of a certain dye solution, colorimetrically measured. For this purpose, Ashley preferred malachite-green, but Stremme and Aarnio found a basic dye as aniline-blue better than acidic dye. Rohland also gets the same result with the latter authors.

In the August number of this journal, last year, I have already given a brief account of the adsorption of aniline-blue by a porcelain clay from the Aizu district in the Province of Iwashiro. Subsequently, I tried the same experiment on the porcelain clays from Seto in the Province of Owari, Tajimi in the Province of Mino, and a kaolin¹⁾ from a locality in Keishonandō, Korea.

The samples from the first two localities belong to the kind of porcelain clay, locally known under the name of "Gairome" and

1) For the Sample of this Kaolin, I am indebted to the Imperial Technical Laboratory, Fukagawa in Tokyo.

“ Kibushi.” Gairome is a redeposited sandy clay, extensively distributed in the intervening valleys and plains in the granodiorite region of Aichi and Gifu Prefectures, and derived from the decomposition of the igneous rock.

Kibushi is a kind of porcelain clay of the same derivation, but subsequently altered under the influence of humic and allied acids of vegetable origin; the Kibushi clay is always found in alternation or in association with lignite seams or seams of “ Kawaki ” as it is locally called, and contains in itself also not a small amount of lignitised substance. This clay is highly refractory, some attaining S. K. 33.

My first experiment to be mentioned in this paper consists simply in taking a definite set of a clay to be tested, ranging between 0.5 gr. to 10.0 gr., into separate bottles of 150 cc content, each containing 100 cc. 1/1000 water solution of aniline-blue. The bottles are shaken for half an hour and then left to settle for a day. After all the clay particles in suspension have finally settled to the bottom of the bottle, adsorbing a certain amount of the dyestuff, the solution, then more or less discoloured, is measured with the Ukena's colorimeter.

Test of 0.5–10 grams washed Gairome porcelain clay from Yamaguchi-mura, Higashikasugai-gori, Owari. with aniline-blue and 100 cubic centimeters of distilled water. (Table I).

Table. I.

No. of Test	Grams dye in 100c.c. of water	Grams of clay taken	Grams dye unadsorbed
1.	0.1	0.5	0.087
2.	"	1.0	0.0661
3.	"	2.0	0.0357
4.	"	3.0	0.03007
5.	"	4.0	0.0000
6.	"	5.0	0.0000
7.	"	7.5	0.0000
8.	"	10.0	0.0000

Test of 0.5–10 grams washed Gairome porcelain clay from Tokiguchi, Prov. of Mino with aniline-blue and 100 cubic centimeters of distilled water. (Table II.).

Table II.

No. of Test	Grams dye in 100c.c. of water	Grams of clay taken	Grams dye unadsorbed
1.	0.1	0.5	0.0816
2.	"	1.0	0.0680
3.	"	2.0	0.0340
4.	"	3.0	0.0012
5.	"	4.0	0.00004
6.	"	5.0	0.0000
7.	"	7.5	0.0000
8.	"	10.0	0.0000

Test of 0.5–10 grams washed kaolin Korea with aniline-blue and 100 cubic centimeters of distilled water. (Table III.).

Table. III.

No. of Test	Grams dye in 100c.c. of water	Grams of clay taken	Grams dye unadsorbed	Remarks.
1.	0.1	0.5	0.0822	measured after several days
2.	"	1.0	0.0714	
3.	"	2.0	0.0423	
4.	"	3.0	0.0016	
5.	"	4.0	0.0000	
6.	"	5.0	0.0000	
7.	"	7.5	0.0000	
8.	"	10.0	0.0000	

Secondly, the same process was repeated on the mixtures of the washed kaolin from Korea, already referred to above, feldspar flour from Amakusa and quartzite flour from Tajimi in the Province of Mino (locally called "Toyaneishi"), in various proportions. Tables IV-VIII show how little is the effect of mixing the feldspar and quartzite flour in the kaolin, in respect to its adsorptive power.

Test of the mixture of the washed kaolin, feldspar- and quartzite flour with aniline-blue and 100 cubic centimeters of distilled water.

Table IV.

No. of Test	Grams dye in 100c.c. of water	Grams of			Grams of the mixture	Grams dye unadsorbed	Remarks
		K.	F.	Q.			
1.	0.1	0.25	0.25	0	0.5	0.0917	K = Kaolin F = Feldspar Q = Quartzite } measured after 5 days
2.	"	0.5	0.5	0	1.0	0.0832	
3.	"	1.0	1.0	0	2.0	0.0785	
4.	"	1.5	1.5	0	3.0	0.0616	
5.	"	2.0	2.0	0	4.0	0.0140	
6.	"	2.5	2.5	0	5.0	0.0070	
7.	"	3.75	3.75	0	7.5	0.0000	
8.	"	5.0	5.0	0	10.0	0.0000	

Table V.

No. of Test	Grams dye in 100c.c. of water	Grams of			Grams of the mixture	Grams dye unadsorbed	Remarks
		K.	F.	Q.			
1.	0.1	0.25	0.125	0.125	0.5	0.0905	} measured after 5 days tinged blue very faintly
2.	"	0.5	0.25	0.25	1.0	0.0843	
3.	"	1.0	0.5	0.5	2.0	0.0773	
4.	"	1.5	0.75	0.75	3.0	0.0604	
5.	"	2.0	1.0	1.0	4.0	0.0211	
6.	"	2.5	1.25	1.25	5.0	0.0151	
7.	"	3.75	1.875	1.875	7.5	0.0000	
8.	"	5.0	2.5	2.5	10.0	0.0000	

Table VI.

No. of Test	Grams dye in 100c.c. of water	Grams of			Grams of the mixture	Grams dye unadsorbed	Remarks
		K.	F.	Q.			
1.	0.1	0.3	0.15	0.05	0.5	0.0357	} measured after 5 days tinged blue very faintly
2.	"	0.6	0.3	0.1	1.0	0.0800	
3.	"	1.2	0.6	0.2	2.0	0.0694	
4.	"	1.8	0.9	0.3	3.0	0.0500	
5.	"	2.4	1.2	0.4	4.0	0.0046	
6.	"	3.0	1.5	0.5	5.0	0.0000	
7.	"	4.5	2.25	0.75	7.5	0.0000	
8.	"	6.0	3.0	1.0	10.0	0.0000	

Table VII.

No. of Test	Grams dye in 100c.c. of water	Grams of			Grams of the mixture	Grams dye unadsorbed	Remarks
		K.	F.	Q.			
1.	0.1	0.4	0.08	0.02	0.5	0.0801	bluish tinged very faintly
2.	"	0.8	0.16	0.04	1.0	0.0712	
3.	"	1.6	0.32	0.08	2.0	0.0577	
4.	"	2.4	0.48	0.12	3.0	0.0113	
5.	"	3.2	0.64	0.16	4.0	0.0001	
6.	"	4.0	0.8	0.2	5.0	0.0000	
7.	"	6.0	1.2	0.3	7.5	0.0000	
8.	"	8.0	1.6	0.4	10.0	0.0000	

Table VIII.

No. of Test	Grams dye in 100c.c. of water	Grams of			Grams of the mixture	Grams dye unadsorbed
		K.	F.	Q.		
1.	0.1	0.2	0.16	0.14	0.5	0.0969
2.	"	0.4	0.32	0.28	1.0	0.090
3.	"	0.8	0.64	0.56	2.0	0.0821
4.	"	1.2	0.96	0.84	3.0	— ?
5.	"	1.6	1.28	1.12	4.0	0.0639
6.	"	2.0	1.6	1.4	5.0	0.0590
7.	"	3.0	2.4	2.1	7.5	0.0087
8.	"	4.0	3.4	2.8	10.0	0.0000

Lastly, the Kibushi clay mentioned in the preceding page was treated in a similar manner.

Test of 0.5-10 grams washed Kibushi clay mixture from Injo, Seto and Toribayashi, Shinano-mura with aniline-blue and 100 cubic centimeters of distilled water.

Table IX.

No. of Test	Grams dye in 100c.c. of water	Grams of clay taken	Grams dye unadsorbed	Remarks
1.	0.1	0.5	0.0808	in order to settle quick small amount of NaCl supplied.
2.	"	1.0	0.0583	
3.	"	2.0	0.0001.....	
4.	"	3.0	0.0000	
5.	"	4.0	0.0000	
6.	"	5.0	0.0000	
7.	"	7.5	0.0000	
8.	"	10.0	0.0000	

Now taking the amount of dye adsorbed in grams for abscissa and of the samples tested for ordinate, we can represent all the results given above on the tables I-IX, on one diagram which is as follows.

Fig. 1. Adsorption of Aniline-blue by

	No. of Curves
Gairome porcelain clay (Table I).....	1
" " " (Table II)	2
Washed Kaolin from Korea (Table III)	3
The mixtures of Washed Kaolin, Feldspar and quartzite flour (Table IV-VIII).....	4-8
Washed Kibushi clay (Table IX)	9

It follows from the foregoing tables that the Kibushi clay has the greatest adsorptive power of all the clays tested above.

On the other hand, the Kibushi clay is known to have the following composition¹⁾:

Ignition loss14.53 (13.20 in the text)
SiO₂50.42

1) This is the chemical composition of a washed Kibushi clay from Huitodo, Seto-machi, in the Province of Owari, as given by Imperial Technical Laboratory. The Kibushi clay here used for the adsorption test is from another locality, but the two clays, I think, do not essentially differ in their chemical composition.

Al ₂ O ₃	33.01
FeO	0.34
CaO	0.34
MgO	0.44
K ₂ O	0.80
Na ₂ O	0.28
total	100.16

and from this we get, by the ordinary method¹⁾ of calculation :

Clay substance ²⁾ =	80.53%
Feldspar substance =	7.508%
Free silica =	8.824%
Ignition loss =	3.296%
total	100.158

Thus, the Kibushi clay which possesses a great adsorptive power is found to contain a large amount of clay substance in it; the result obtained is very natural, for we can easily expect from the proposition set forth at the beginning of this paper that the adsorptive power of a clay may give a direct measure of the amount of the clay substance in it.

On the foregoing diagram showing the relative amount of the adsorbed dye we see Nos. 1, 2, 3, and 9 represented by an almost straight line while Nos. 4, 5, 6, 7, and 8 are very irregularly curved. What the difference indicates is naturally quite simple; the quartz- and feldspar flours which are taken as admixture into the washed kaolin are mostly not in colloidal dimension.

At the end of this report, I am going to add another table on which is given the adsorptive power of various clays for aniline-violet and aniline-blue; of various clays used in this test, most kinds of Kibushi clay and washed Gairome porcelain clay are found to have the greatest adsorptive power.

1) Journ. of Ceramic Society of Japan, Jan., 1915, 213. (Trans. from Brick and Clay Record Sept. 1914. by Mr. Yamada).

2) Clay substance = Al₂O₃. 2SiO₂. 2H₂O.

Test of each 2.5 grams of various clays with 0.15 grams of aniline-blue and aniline-violet in 50 cubic centimeters of distilled water.

Table X.

Designation of Clay	Portion unadsorbed		Remarks
	Aniline-violet	Aniline-blue	
1. Kibushi clay, Haito, Seto	—	0.0000	tinged very faint blue.
2. " Injo, Sto	0.000247	0.0000	
3. " Toribayashi, Shinano-mura, Owari	—	0.0000	
4. Washed Kibushi of mixture (2) and (3)	0.00017	0.0000	
5. Gairome, Goizuka, Shinano-mura, Owari	0.02250	0.01704	coagulation very slow.
6. Washed Gairome, " "	—	0.0000	
7. Gairome, Shiokusa, Akatzu-mura, Owari	0.02387	0.0150	
8. Washed Gairome, the same locality	0.00030	0.0000	
9. Gairome, Yamaguchi-mura, Owari	0.03750	0.0250	
10. Special washed Gairome, " "	0.00015	0.00000	
11. Gairome (a), Tokiguchi, Mino	0.009204	0.00379	
12. " (b), " "	0.02250	0.01636	
13. " (c), " "	0.02625	0.01704	
14. Special washed Gairome, " "	0.00015	0.0000	
15. Washed Gairome (a), Tokiguchi Mino	—	0.0000	
16. " " (b), " "	0.00015	0.0000	
17. Shiraedo, Matsumoto, Kozoji-mura, Mino.	0.000392	0.0000	
18. " Ohari, Karu-gori, Mino.	0.010227	0.01227	
19. Kaolin, Pennsylvania	0.03375	0.01772	
20. " Carlsbad in Bohemia	—	0.01772	
21. " Korea	0.01875	0.03977	
22. Washed kaolin, Korea	0.000323	0.03636	
23. " feldspar, Takamine, Naegi, Mino	0.023864	0.06818	