NOTES AND NEWS

ON THE ADSORPTION OF SOME ORGANIC DYES BY CLAYS AND CLAY MINERALS

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In recent years this subject has been investigated from various points of view. In an attempt to discover fundamental laws governing some of the anomalies, I have been concerned mainly with the quantitative aspect and microscopic examination. German investigators before the war tried to correlate the adsorption of malachite green, for example, with oil decolorization. My work has been confined to reactions between identified specimens, and wherever possible to clay minerals, and a limited number of organic compounds. This is absolutely necessary in a study of this character as even the purest type of clay, kaolin, always consists of at least two minerals, namely quartz and kaolinite. Bentonites, at least those examined, have a glassy phase present in varying amounts. More often than not limonite, hematite, feldspars, and hydromicas are present as well in kaolins, etc. *X*-ray determinations by Dr. R. E. Grim have shown the presence in South African fireclays of montmorillonite. Usually regarded as almost solely composed of kaolinite as the clay mineral and as tests of the benzidine reaction are of little value in this case, more discriminating work is necessary. In South African soils the swelling types of montmorillonite, and especially illite, are far commoner than generally suspected. This is very important from the soil mechanics point of view.

A microscopic examination of the coarser separates from a mechanical analysis often shows that the adsorption is not uniform on the grains. When dealing therefore with such complex reactions one must build on a sound foundation. The results of Hauser and Leggett (1), for example, cannot in my opinion be widely accepted because the clays used in their investigations are not specified in any way.

A. Quantitative Determinations

In Table 1 the chemical analyses of two rocks are given. The Wyoming bentonite is an identified sample, the rough analysis showing it to have a similar composition to the one quoted later in this paper. Any one familiar with the chemical composition of clays is aware of the care that must be exercised when describing these rocks as "a dried sample." A considerable amount of water is driven off from temperatures of 105°C. upwards and it is very difficult to draw a sharp distinction between moisture and combined water, especially in the case of montmorillonite-bearing clays. A sample dried at temperatures of 105° to 110°C. has still a considerable amount of water present which may take part in the reactions Hauser and Leggett investigated.

TABLE 1

	1.	2.
SiO_2	44.40	46.38
Al_2O_3	38.10	36.58
Fe_2O_3	3.80	0.88
TiO_2	0.09	0.31
CaO	0.06	0.60
MgO	tr.	0.49
Na_2O	—	0.04
K_2O	—	0.88
Loss on Ignition	12.85	12.22
H_2O	—	0.67
	99.30	99.05

1. Kaolin, White River, Transvaal. *Analyst V. L. B.*
2. Purified kaolin supplied by Wengers Ltd., Stoke-on-Trent. *Analyst V. L. B.*

Working with the dyes malachite green, congo red and methyl violet, the adsorptive powers were tested on these two clays as well as on the bentonite. Aqueous solutions were used throughout with a concentration of 0.025%. Previously (2) I had shown that in two hours contact over 90% of the dye was adsorbed. In these experiments at least 24 hours contact was allowed to ensure "satisfaction" of the clay's adsorption powers. In Table 2 the results are summarized.

TABLE 2

Clay Type	Amount of dye adsorbed in gms. per gram of clay		
	Malachite green	Congo red	Methyl violet
Kaolin, Stoke-on-Trent	.0074	.0081	.0083
Kaolin, Natal	.0068	not. det.	not. det.
Kaolin, Transvaal	.0082	.0073	.0083
Bentonite, Wyoming	.036	.045	.047
Montmorillonite-rich fraction, S. African clay. Potchefstroom.	.050	not det.	not det.

Bearing in mind that the samples are not pure, the inference can be made from these results and for these samples at least, that the amount of dye adsorbed is dependent upon the clay type, that is, it is a function of its chemical and mineralogical composition. The grain size appears to be of little importance.

No difficulty was experienced in getting clear filtrates except in the case of the Stoke-on-Trent kaolin which had been stained by Congo red. In this case several layers of the finest Whatmans No. 542 paper proved satisfactory.

The results indicate that there is a limiting value for each clay type. If this can be shown to apply generally then such quantitative determinations may be of considerable value in the study of clays and soils.

B. Qualitative Determinations

In this part of the research only analyzed specimens were used for the critical work. In a few cases to complete the tables and only where negative color reactions were obtained, specimens which had not been analyzed were used. All these tests were carried out on small quantities, that is spot tests. Frequent examinations under the microscope were made in order to observe if it was a "whole hearted" reaction and not a portion of the rock which was giving the color change. Owing to the difficulty of obtaining the reagents only a few compounds were used to continue the work of Hauser and Leggett. The illite and montmorillonite specimens were obtained from Dr. R. E. Grim of the Illinois Geological Survey. The amounts of these were too small to permit quantitative determinations.

The qualitative work can be divided into two parts:—

(1) The use of naturally colored dyes as malachite green, methyl violet, congo red, fuchsin basic, etc. All the clays examined in the course of a survey of the Union of South Africa and amounting to about four or five hundred samples, adsorbed these compounds in varying amounts. Note that the color is stable on drying.

(2) The use of colorless or only slightly colored amines as *o*-toluidine, benzidine, diphenylamine, aminoazobenzine, etc. Only the montmorillonite or illite-bearing specimens reacted. The colors fade or disappear altogether on drying. (See Tables 3A, 3B, and 4.)

TABLE 3A

Specimen	Natural Color	*p*H	Group 1 Reagents			Group 2 Reagents		
			Malachite green	Congo red	Methyl violet	Benzidine	*o*-Toluidine	Diphenylamine
Kaolinite, Middleburg, Transvaal	White	7.0	+	+	+	— Wet or	— dry no rea	— ctions.
Kaolin, White River	White	6.0	+	+	+	—	—	—
Kaolin, Stoke-on-Trent	White	7.0	+	+	+	—	—	—
Fireclay, Glenboig	Lead gray	7.0	+	not. det.	not det.	—	—	—
43–2μ Fraction of Kaolin	White	not det.	+	+	+	—	—	—

VOLUMETRIC COMPOSITION

Kaolinite	82.7
Quartz	5.7
Muscovite with some biotite	11.4
Iron oxides	0.1
Feldspars	tr.
	99.9

CHEMICAL ANALYSIS

SiO_2	50.3
Al_2O_3 Fe_2O_3	32.0
Loss on ignition	11.1
	93.4

Assuming the remainder of this analysis as K_2O and recalculating on this basis gives a surplus of 6.6% free silica, thus corresponding well with the micrometric value of 5.7%.

Analyst V.L.B.

The grains in this specimen when examined under the microscope exhibit "zoning" due to adsorption of the dyes.

TABLE 3B

Specimen	Natural color	*p*H	Group 1 Reagents			Group 2 Reagents		
			Malachite green	Congo red	Methyl violet	Benzidine	*o*-Toluidine	Diphenylamine
Illite, Illinois	Dirty shale	7.0	+	+	+	Prussian blue	Dirty green, not distinct	—
Illite, Goose Lake	Dirty shale	7–8	+	+	+	Prussian blue	Dirty green	—
Bentonite, Wyoming	Dirty white	7–8	+	+	+	Prussian blue, deep.	—	—
Montmorillonite, Wyoming	Pale buff	7–8	+	+	+	Deep prussian blue.	—	—
Activated fuller's earth	Dark buff	>4.0	+	not det.	not det.	—	Brownish Color?	Dirty green
		>8.0				—	not det.	not det.

Note. In all these tests using group 2 reagents the materials were mixed dry (at 110°C.). In no case could any reaction be seen. On wetting the reaction proceeded in the case of benzidine. The observations on fuller's earth are incomplete, but the reactions appear to be similar to the rocks predominantly composed of kaolinite.

TABLE 4

Specimen	Benzidine	Aminoazobenzine	Nitrophenol
Natrolite from Berg basalt, Natal. Dept. N. U. C. no. 528	Dry, nil Wet, nil	No discernible reactions, wet or dry	No reaction discernible
Kaolin Ndedwe from N. U. C.	Dry, nil	No discernible reactions	No reaction discernible
Zeolite (?), S.W. Africa. Natal Museum no. 1671	Dry, nil Wet, nil	No discernible reactions	No discernible reactions
Bentonite, Wyoming, obtained from Dr. F. C. Tompkins	Dry, nil Wet, deep prussian blue	No discernible reactions	Intense canary yellow coloration, different from the color of the nitrophenol

The glassy material in the bentonite shows no reaction at all with any of these reagents.

A study of these results shows three important facts.

(1) All the clay minerals adsorb the dyes of group 1 listed above, in varying amounts. The dye once taken up by the clay mineral is relatively fixed. The color however can be changed by varying the *p*H.

(2) The color reaction of benzidine appears to be confined to illite and montmorrillonite. Kaolinite at any rate does not show any color reaction. This is very important as Page (4) has doubted the validity of the benzidine test for montmorrillonite in soils advocated by Hendricks and Alexander (5).

(3) The *o*-toluidine reactions are not as distinctive as the benzidine ones.

Since completing this work, I carried out some additional tests at Natal University College at Pietermaritzburg. Working on a bentonite from Wyoming, I obtained further interesting results. I am indebted to Dr. F. C. Tompkins of the Department of Chemistry for the specimen and also for the following analysis:—

SiO_2	61.78
Fe_2O_3	3.10
FeO	0.28
MnO	0.08
Al_2O_3	21.56
CaO	0.68
MgO	2.62
K_2O	0.31
Na_2O	2.22
SO_3	tr.
H_2O (110°C.)	3.10
Ignition loss	4.73
	100.46
S.G.	2.0

Analyst unknown.

This sample of bentonite, composed mainly of montmorillonite, but also containing small proportions of a glassy phase, reacted with benzidine in the normal manner. The glassy phase under the microscope showed no change in color after the benzidine had been added. Substituting ethyl alcohol for water, no color reaction was noted. Upon the addition of water the color developed immediately. The color reaction, therefore, depends upon ionization and can only take place in the presence of water which is not combined in the clay mineral complex. Dr. F. C. Tompkins pointed out the resemblance between this and the iodine coloration of starch in the presence of potassium iodide. I tried out dilute solutions of iodine in potassium iodide aqeous solutions and found that the blue color was destroyed on drying, but returned on wetting again. This process could be repeated a number of times. It would appear that these phenomena are of the same kind.

With regard to Page's criticism of the test of benzidine for montmorillonite, I would point out that many of the kaolins examined contained over 0.5% ferric oxide and the Transvaal one nearly 4%. The activated fuller's earth besides being very acid contains appreciable quantities of ferric oxide. Page emphasizes the part played by Fe^{+++} in the production of color and postulates that this phenomenon may be due entirely to the ferric ion and not to the clay mineral at all. My results show that even in the presence of appreciable quantities of ferrous and ferric oxides, in the case of kaolins, no color reaction takes place.

Dr. L. C. King of the Department of Geology, Natal University College, placed at my disposal several specimens of zeolites. Although these have not been critically determined, as the results were negative, I have included them to indicate the direction of the work. While it would appear that the zeolites are not very reactive, more detailed work is necessary before any conclusions can be made. The same applies to pyrophyllite.

C. Conclusions

From these experiments it would appear that the two types of reactions, although probably of the same kind, are different in their outward results.

(1) The stains are fixed in the mineral constitution. The reaction is apparently irreversible.

(2) Color reactions which may be due to resonance set up by various ions and the organic compound. "Removal" of the water destroys the color, addition of it restores it.

Acknowledgments

I am indebted to Drs. L. C. King, F. C. Tompkins, Lawrence, and R. E. Grim for specimens.

References

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