

NOTES AND NEWS

FURTHER NOTES ON THE ADSORPTION OF MALACHITE GREEN BY SOME CLAY MINERALS

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In a recent note (1) on this subject I drew attention, among other things, to the fastness of the dye taken by certain clay minerals, and also to the varying amounts of the staining compound adsorbed. Since then my attention has been drawn to a comprehensive paper by Faust (2) on the staining of clay minerals. This is one of the most detailed papers published and deals fairly extensively with the technique of staining. Hauser and Leggett (3) describe the color reactions between amine compounds and various clays. Some of the clays used in the latter research are undoubtedly mixtures of minerals, so that the results may not be sufficiently discriminating for microscopic work. However, it is with the quantitative aspect that I am more concerned and in this note some results are given, which although incomplete suggest a fertile field of research. All the tests described here were done on the raw clay minerals, but Professor S. J. Shand, in a private communication, suggests combining staining with partial dehydration of the clay minerals. In view of the differing thermal behavior of kaolinite, montmorillonite, anauxite, etc., this method may be useful. Active service prevented any experimental work in this direction.

TECHNIQUE USED IN THIS INVESTIGATION

Aqueous solutions of 0.01 to 0.05% of malachite green were used throughout the work. The minerals were stained at ordinary room temperatures, and were carefully washed to remove all excess stain for qualitative work. In all the quantitative work, loose grains of varying sizes from 200 to 10 microns in diameter were used. In the qualitative examinations thin sections of previously stained chips were examined, but size separates from mechanical analyses formed the bulk of the material studied. The six separates after drying at 110° C. were mounted in kolloid or oils. Note that unlike the aqueous amine staining reactions, *drying does not alter* the color. Only thermal destruction of the malachite green at temperatures in excess of 600° C. can remove the color. In fact as far as can be ascertained, in the case of certain of the clay minerals the reaction between malachite green and the aluminum silicate hydrates is irreversible.

In the quantitative investigations, 10 cc. of 0.05% solution were added

to 1 gram of the sample and allowed to remain in contact for varying periods, with constant stirring. The supernatant liquid was then decanted on to a very fine filter paper (Whatmans 541) and the concentration determined colorimetrically. If the stained particles were to be examined microscopically they then were thoroughly washed with hot distilled water until free from stain. In this manner the amount of dye adsorbed could be determined and its effect on the optical properties noted.

QUANTITATIVE DATA

1. *Montmorillonite*

A swelling type of montmorillonite fraction, obtained from a South African clay, was one sample studied in detail. This sample had been previously purified by sedimentation by Professor G. H. Stanley. The specimen which was a rather dirty green in color was freed from particles greater than about 40 microns and exhibited the characteristic swelling on the addition of water. Its powers of decolorizing were noted to be very high. The chemical composition was found to be as follows:

SiO ₂	55.45
Al ₂ O ₃	11.47
Fe ₂ O ₃	8.60
TiO ₂	0.06
MnO	tr.
CaO	0.85
MgO	2.97
Loss on ignition	12.46
H ₂ O—	7.42
	99.28

Analyst V.L.B.

The relationship between adsorption and time is shown in the curve, Fig. 1. The concentration of the filtrate decreases rapidly in a few minutes. The reaction velocity even in the case of large particles is very high. In addition, this clay is capable of decolorizing very strong solutions in a short time. Even coarse particles of this montmorillonite are capable of strong adsorption.

2. *Kaolinites*

The kaolinites studied adsorbed far less malachite green but held it just as strongly. In fact it is a characteristic of kaolinite and the bentonitic minerals, that the dye is fast. Some of the minerals studied, notably anauxite and pyrophyllite, exhibit these properties to a smaller extent. Pyrophyllite is quite a common constituent in certain residual clays and the specimen about to be discussed was possibly contaminated by it.

A white residual kaolin from the Eastern Cape Province was analyzed mechanically. The "fine sand" fraction was very uniform in size and was used in the stain tests. The composition was found to be as follows:

SiO ₂	78.00
Al ₂ O ₃	14.70
Fe ₂ O ₃	1.37
TiO ₂	1.59
MnO	nil
CaO	0.30
MgO	nil
Loss on ignition	4.30
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	100.26

Analyst V.L.B.

Using a 0.05% solution as before and an adsorption period of ten minutes, the sample was found to take up 0.0068 gram of malachite green per 1 gram of clay, i.e. about 32% of the dye added was adsorbed. Under the microscope the aggregate was found to be stained a rather greenish-blue and only a few of the particles took the dye, becoming slightly pleochroic. Numerous platy and fibrous minerals of refractive index greater than 1.54 were noted which did not stain at all. Another point observed was that many grains stained differentially, i.e. the intensity of the dye varied in the same grain. In fact particles were observed which were not stained at all on one side and were greenish-blue on another.

A fine, white, powdery kaolin from Natal was also examined. This clay exhibited the rather rare phenomenon among specimens of its type of changing color upon the addition of water. The clay changed from a fairly flat-white to a creamy-yellow on damping. The chemical composition was found to be as follows:

SiO ₂	49.88
Al ₂ O ₃	33.47
Fe ₂ O ₃	2.73
TiO ₂	1.30
MnO	nil
CaO	0.55
MgO	0.04
Loss on ignition	12.82
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	100.79

Analyst V.L.B.

As this material was to be tested for industrial use the procedure was to employ the entire sample in the experiment, and not any sized portion. A size analysis by pipette and sieves gave:

<i>Size in microns</i>	<i>Per cent by weight</i>
> 589	0.5
589-200	2.9
200- 88	3.0
88- 74	4.2
74- 61	1.4
61- 43	1.6
43- 31	0.6
31- 16	80.0
16- 11	2.3
< 11 (by difference)	2.71
Moisture at 110° C.	0.79
	100.00

The absence of colloidal material will be noted. In fact South African kaolins are remarkable for their high proportion of crystalline kaolinite and absence, or negligible amount, of colloids present. In the coarser fractions of this clay there was abundant kaolinite, some muscovite and quartz, pigmented by small amounts of limonite. Using the same adsorption conditions the following results were obtained:

Time in mins.	Concentration of filtrate % malachite green
1	0.0078
5	0.0055
10	0.0039
60	0.0037
120	0.0035

The rapidity of the reaction will be noted again. Over 90% of the dye is adsorbed in ten minutes.

3. *Pyrophyllite*

A white, flaky specimen from North Carolina was obtained and as can be seen from the analysis was very pure, a fact confirmed by microscopic examination.

The malachite green stained it sky-blue. On drying, the color is not altered but immersion in kolloid imparts a distinct bluish-green color, very similar to kaolinite. The particles show no distinct pleochroism and exhibit aggregate polarization.

SiO ₂	65.74
Al ₂ O ₃	27.71
Fe ₂ O ₃	0.21
TiO ₂	0.41
MnO	nil
CaO	0.12
MgO	0.02
Na ₂ O	0.60
K ₂ O	0.18
Loss on ignition	4.90
H ₂ O—	0.29

 100.18

Analyst V.L.B.

It should be noted, as in the other two cases of kaolinite and montmorillonite, the color of the stained particles can be changed from blue to red on the addition of any acid, such as hydrochloric (i.e. shades of either color depending upon the mineral), and vice-versa on adding alkali. These reactions can also be effected on the dried aggregates by the fumes of ammonia or hydrochloric acid. Furthermore there does not appear to be a limit to the number of times these operations can be performed.

4. *Massive Sample of Montmorillonite*

A specimen of a pure white, massive montmorillonite was obtained from Arizona. A partial and rather rough analysis is given below. The alumina was determined directly by the 8-hydroxy-quinoline method.

SiO ₂	49.48
Al ₂ O ₃	8.28
Fe ₂ O ₃ }	9.82
TiO ₂ }	
CaO	2.16
MgO	6.32
Loss on ignition	8.68
H ₂ O—	17.42

 102.16

Analyst V.L.B.

The sample becomes uniformly dark blue on staining. The mineral after this treatment does not exhibit pleochroism, and on acidifying becomes a deep salmon-red. The specimen did not adsorb as much malachite green as the swelling variety, the actual amount being 0.0074 gm. per gm. of sample.

REMOVAL OF EXCESS MALACHITE GREEN

One specimen after staining was washed continuously for five days with hot distilled water and the filtrate still contained small amounts of the dye. The conclusion was reached in this case that the material under examination was yielding again the malachite green, but at a very much slower rate than it adsorbed the dye. The chemical composition was found to be:

SiO ₂	88.70
Al ₂ O ₃	7.40
Fe ₂ O ₃	2.16
TiO ₂	tr.
MnO	nil
CaO	0.26
MgO	0.11
Loss on ignition	1.64
	100.27

Analyst V.L.B.

This sample was a "fine sand" fraction from a residual, dirty kaolin (specimen D. 88) from the Grahamstown district, Cape Province. It contained much free silica in the form of quartz, but this did not take the stain, not even along the cracks.

QUALITATIVE DATA

Besides the quantitative data described above, more than a hundred stained aggregates have been mounted and examined. Thin sections of the harder clays have been prepared, and in each case a stained and unstained section were compared microscopically. Some qualitative and quantitative work was also done on the light absorption, before and after staining. Attention was paid in particular to the blue and violet end of the spectrum.

CONCLUSIONS

In most cases the remarkable fastness of the dye is noteworthy. The stability of it is great and stained particles can be heated and mounted in resins without difficulty. The stained particles can also, after drying, be examined by immersion in the oils described recently (4).

A considerable amount of work remains to be done on these minerals. Illite, dickite, and auxite have only been subjected to cursory examination and so far no data is available for nontronite and the ferruginous clay minerals. Illite was found to be present in one of the specimens of kaolin-ite, but only in small quantities.

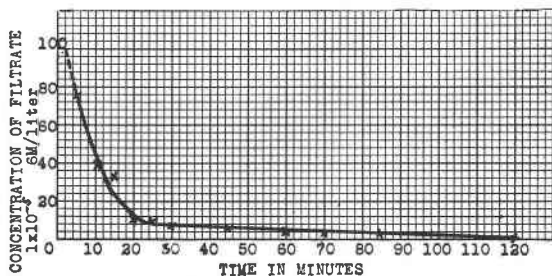


FIG. 1. The concentration of the malachite green in this experiment was 0.025 per cent. 100 cc. were added to 0.5 gm. samples. Small samples of clay had to be used as the amount of material was small. It will be noted that 99.9 per cent of the dye is adsorbed at the end of two hours.

REFERENCES

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