

# THE COLOURATION OF MONTMORILLONITES AT VARIOUS pH VALUES

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In view of the fact, that the demonstration of minerals in clays is even in a well equipped laboratory a complex task different methods have been elaborated for this purpose. Each has its advantage and disadvantage. The advantages involve the estimation being as quick as possible, the furnishing within a certain limit of error of suitable data concerning the different types and that the method does not require a too expensive equipment. From this point of view the staining procedures used for the determination of clay minerals are certainly advantageous.

However, the estimations based on the colour reaction can only be advantageous if they can easily be reproduced showing a characteristic colouration of the different mineral samples which is intensive enough to be easily detected. It is important that the colouration due to the colour reaction should differ distinctly from the original colour of the mineral. It is essential that the staining procedure should not require much preparation and that the produced colour should remain constant at a wide pH value range. If these conditions are assured it facilitates the application on the site to a great extent. Of course, if we also succeed in determining the clay mineral group by means of the staining procedures for the more precise results more detailed investigations are required.

In the preliminary report<sup>5</sup> several organic compounds have been described with which an intensive colouration of clay minerals, in the first place montmorillonite, can be carried out. However, it remained an open question to what an extent the change of the pH value influences the produced colour, whether or not the cation exchange exerts an effect and if so how it influences the colouration. In view of these facts at the investigations these circumstances were dealt with in the first place. Different authors have observed that clay-suspensions prepared with solutions of organic substances change their colour according to whether the medium is acid or basic.

In his investigations V. L. Bosazza<sup>1</sup> took the change of the pH value to such an extent into consideration that he gave the pH value of the

suspension prepared with water within wide limits. On the other hand, he points to the fact that by variation of the pH the produced colour may be changed to a certain extent.

In their paper *S. B. Hendricks* and *L. T. Alexander*<sup>4</sup> established definitely that the hydrogen ion concentration is not essential although they admit that in moderately acid medium, i. e. at lower pH values they obtained with benzidine green colours.

*E. A. Hauser* and *M. B. Leggett*<sup>5</sup> dealing with organic compounds producing colouration mention colours produced in acid and basic mediums.

*R. C. Mielenz*, *M. E. King* and *N. C. Schieltz*<sup>6</sup> using previously treated clays and samples respectively, always worked if possible with neutral values.

*R. C. Mielenz*, *M. E. King*<sup>7</sup> observed the change of the colour of montmorillonite in relation to the change of the pH value of the suspension. The solution was acidified with 0.05 N HCl. At pH ranges of 10.8—0.0 they detected the same colours as the author of the present paper.

*M. M. Sukevitch*<sup>10</sup> examined at lower pH values the colouration produced by methylene blue in connection with the change of the pH value in the presence of KCl. According to him in the case of caolinite the change of the pH value does not influence the colour.

*M. F. Vikulova* mentions as a deficiency of the investigations upto date that the Russian investigators<sup>12</sup> do not take the change of the pH value into account.

These references prove too that the colour reactions due to the change of the pH value essentially influence the colour of the suspension. It is natural, therefore, that by controlling the value of the pH the suitability of the colour reaction can be enhanced.

The colour of the clay mineral suspensions prepared with organic compounds used by the author and described in a previous paper also exhibited a considerable change in correlation with the pH. In order to elucidate this question investigations were carried out not only with the previously used benzidine, orthotolidine and diphenylamine but also with orthotolidine, orthophenylenediamine and paraphenylenediamine which under certain conditions proved to be suitable specific substances for the determination of montmorillonites. The pH measurements were carried out with an electric pH meter. The produced colours were brought into relation to the basic colours of the *Unesma*<sup>11</sup> colour scale. The wave lengths of the basic colours — which were not typical mixed colours — were determined by means of a *Zeiss* spectro-photometer. This was carried out in order to render possible the plotting of the colour changes depending upon the pH value on a diagram. The pH value was plotted on the one axis and the numbers corresponding to the *Unesma* colour scale on the other one in a sequence that the lower part of the diagram showed the colours with lower wave lengths, whilst for the orientation of the reader the approximative wave length of the basic colours were also denoted. The pH of the suspensions was either higher or lower than the H ion concentration of their filtrates, in the case of electropositive particles the H ion concentration of the suspension is smaller. The difference between the H

ion concentrations of the filtrates and suspensions was in proportion with the amount of the particles in the suspension.

The behaviour of the most generally used benzidine in aqueous solution is as follows. In water it is very insoluble thus practically it can only be prepared as a solution of 0,01 per cent. Although the reaction also takes place in the case of such a low dilution yet it proved to be better if the benzidine was introduced in excess as then the reaction ran down more rapidly and the colour was also far more intensive. The change of the pH

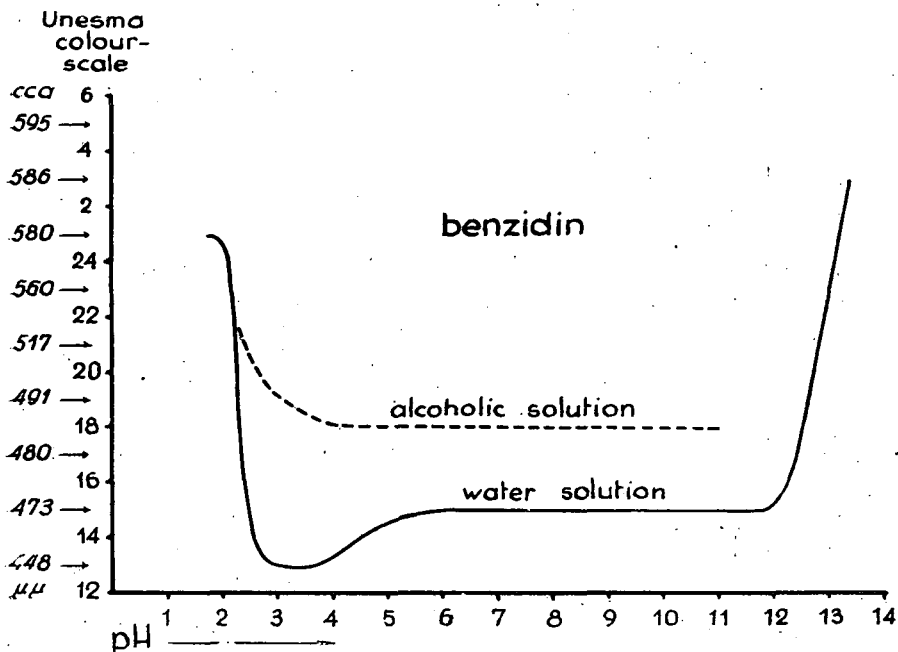


Fig. 1.

values of the suspensions was carried out with 0.1 N HCl and 0.1 N NaOH, 1 N NaOH, respectively. The investigations showed that the pH produces in a comparatively wide range 5—11 the characteristic Prussian blue colouration (Fig. 1).

In the basic range it turns gradually from green into light ochre which was difficult to illustrate on the colour scale because it is a mixed colour. In the acid range the appearance of the purple blue colour is characteristic at pH 2.8 it suddenly turns into yellow, in this case therefore the change is not gradual like in the basic range.

If alcohol is used as solvent there was a divergence inasmuch as instead of the characteristic Prussian blue a greenish-blue colour appeared in the range pH 5—11, i. e. a colour with a longer wave length.

For the determination of the montmorilloite group orthotoluidine also seems to be a good specific reagent. In practice it proved to be suitable if a quantity of the substance corresponding to a solution of 1 per cent

was introduced into the solvent independently whether or not the substance had dissolved in the solvent. In this case orthotolidine dissolved in alcohol showed a deep in a range of pH 4.6—12 green colouration, with the aqueous solution the colour produced was somewhat darker (Fig. 2).

At low pH values till the appearing of the yellow colour (1.6 pH) a gradual transition from light green to yellowish green could be observed. In aqueous solution this could not be detected, or at least not to such an extent as when an alcoholic solvent was used. Also in the case of a higher

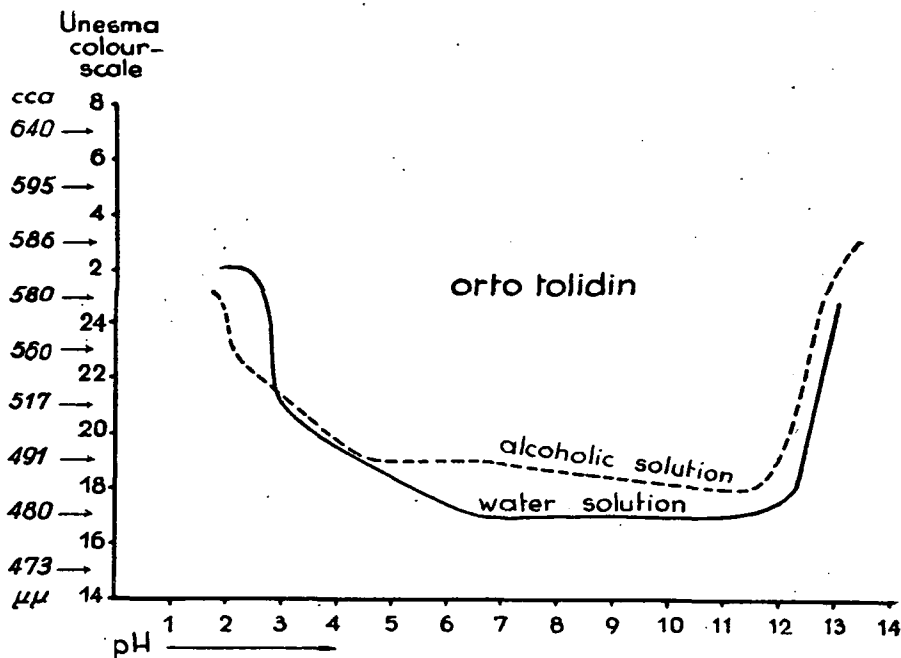


Fig. 2.

pH alcoholic orthotolidine proved too to more suitable. Till pH 13.6 a gradual transition from brownish yellow could be observed, whereas in an aqueous solution over pH 13 a greenish brown and eventually a brown colouration appeared.

For the preparation of montmorillonite suspensions an alcoholic and benzeneous solution of diphenylamine was used. The use of the alcoholic solution is comparatively restricted as it only shows colour reactions at low pH values. The green colouration appearing at pH 1.6 gradually fades as the pH rises it turns into yellowish green, whilst at values over pH 5.5 the montmorillonite did not show any more any changes (Fig. 3).

The montmorillonite suspension prepared with diphenylamine dissolved in benzene did not either change its colour at relatively fairly wide ranged fluctuations of the pH value. In the natural range it is very suitable,

Considering that benzene does not mix with water the measurement of the pH value must be carried out with great care.

Experiments were also performed with orthophenylenediamine and paraphenylenediamine. *E. A. Hauser* and *M. B. Leggett*<sup>3</sup> also mention that these two organic compounds produce colour reactions with clays. *S. B. Hendricks* and *L. T. Alexander* also refer to this, but do not give any details concerning the behaviour. Under certain conditions both substances can be used for the determination of montmorillonites. It is, however, essen-

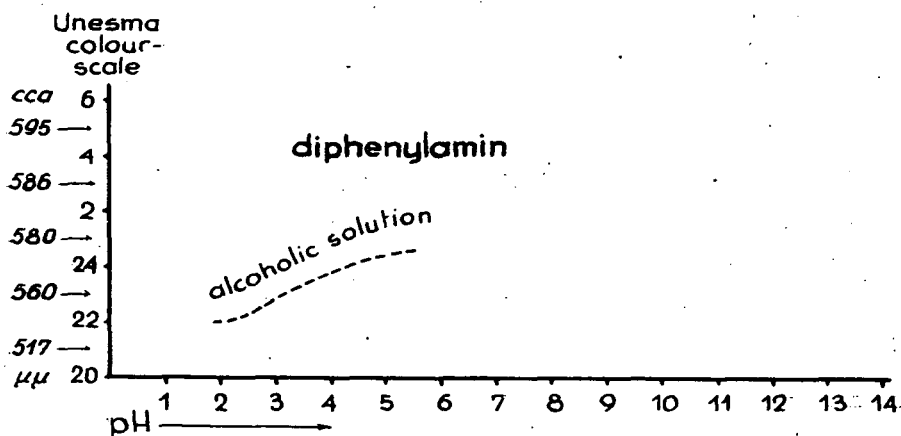


Fig. 3.

tial that only so much solution is prepared from the reagent which is used up as both its aqueous or alcoholic solutions turn relatively quickly yellow or brown respectively, and this interferes with the detection of the colour reaction.

The colour of the suspension prepared with an aqueous solution of orthophenylenediamine showed depending upon the pH values the following changes. At low pH values (1.3—4.5) a uniform violet red colour appeared similarly a relatively characteristic colour could be observed at 7—11 pH, at the most, the brownish red faded. At pH 4.5—7 values transitory colours with brownish shades can be detected. Particularly at low pH values a vivid uniform colour could be observed (Fig. 4).

The montmorillonite suspension prepared with an aqueous solution of paraphenylenediamine behaved in an interesting manner in the course of the pH changes. With freshly prepared solutions a vivid blue colouration appeared in the neutral zone. This colour faded gradually from pH 5 downwards. In the basic range the fading could also be observed from pH 8 on. At neutral pH values the colouration changed comparatively quickly turning from violet blue to a quite dark shade. If the solution was not freshly prepared, but had been stored for at least one day, it showed quite a different colour reaction, between pH 1.5—2.5 values a dark red, lilac redish colour appeared turning eventually within relatively low pH limits gradually green pH 4.5—6.5. With a further increase of the pH

values the colour of the suspension changed to lacmus blue (pH 7.2—9.0) turning at pH 9.5—12.5 into dark violet. It was interesting that in this case the lilac colour appearing at low pH values changed after about 24 hours standing into blue-like in the neutral pH range — although its pH value did not change considerably.

One of the problems of determinations based on colour reactions is that, as is well known, clay minerals readily adsorb different substances and are capable of exchanging certain cations or anions, thus these adsor-

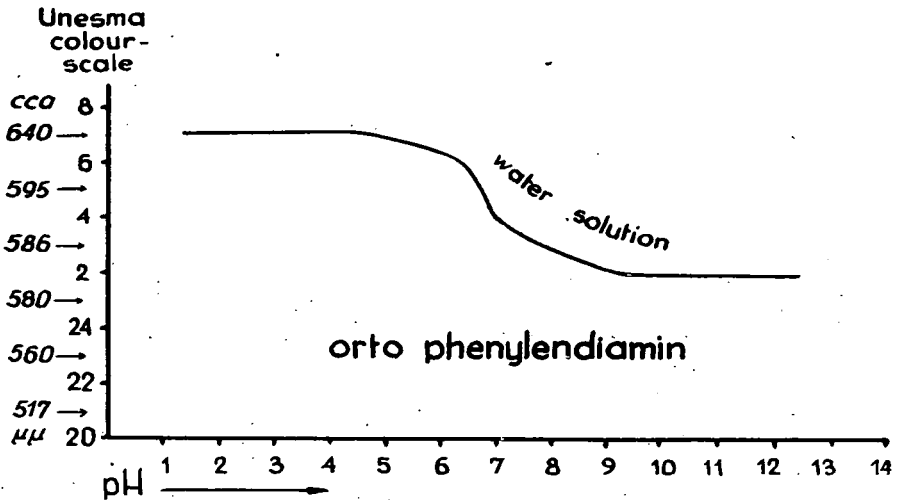


Fig. 4.

bed foreign cations — which are actually impurities — may shift the colour reaction in a direction which does not correspond to the real facts.

W. W. Hambleton and C. G. Dodd<sup>2</sup> have established that the adsorbed exchangeable cations do not play a decisive role regarding the colouration, although according to these authors it seems desirable to remove the  $Fe^{+++}$  salts and  $MnO_2$  exerting an oxidising effect, however, as a result of this treatment with HCl the hectorite and certain nontronites decompose.

According to the above authors only the montmorillonites containing small amounts of  $Fe^{+++}$  iron did not give a good colour reaction, as the colouration due to benzidine only ensued if suitable  $Fe^{+++}$  iron impurities were present in the clay.

For the determination of montmorillonites by means of colour reactions so far almost all investigators used benzidine. The benzidine shows a colour reaction in the presence of soluble  $Fe^{+++}$  salts. In view of the fact that chemical analyses sometimes demonstrate in clay minerals, particularly in the case of montmorillonites, the presence of considerable amounts of  $Fe^{+++}$  the conclusion was drawn that benzidine cannot be a specific substance for the determination of montmorillonites. This view was particularly advanced by J. B. Page<sup>3</sup> who believes that it is not at all

suitable for this purpose. Nevertheless *W. Siegl*<sup>9</sup>, *E. A. Hauser* and *N. B. Leggett*<sup>3</sup>, *R. C. Mielenz*, *M. E. King* and *N. C. Schieltz*<sup>6</sup>, *R. C. Mielenz* and *M. E. King*<sup>7</sup> and others, as well as the author of the present paper, consider it is to be suitable for the determination of montmorillonites, although it should be born in mind that the presence of smaller or larger amounts of  $\text{Fe}^{+++}$  may influence to a certain extent the colour reaction. *V. L. Bosazza*<sup>1</sup> on the other hand, carrying out investigations of clay originating from South-Africa noticed that kaolins, although they contained considerable amounts of ferrous and ferric iron, did not produce colour reactions.

Taking all these facts into consideration experiments with hydrogen montmorillonites — in which case all exchangeable cations are substituted by hydrogen — were performed in order to establish whether or not they produce with the different reagents the characteristic colour reaction and also to elucidate the role of the exchangeable cations. Previously, however, careful examinations were conducted to establish whether the different cations or reagents undergo any reaction with benzidine, orthotolidine, ortho- and paraphenylenediamine and diphenylamine? Of course, the change of the pH values was also taken into account.

The examinations showed the following results:

The first and most striking result was that in the presence of the various amines the hydrogen montmorillonites exhibited the same colour reactions as the ordinary bentonites do, i. e. like the material from Gönc, Istenmezeje etc. Thus in the case of an aqueous benzidine solution the characteristic blue colour, in that of orthotolidine a dark green one and with paraphenylenediamine the dark blue colouration appeared, the latter changed quickly into a violet shade, with orthophenylenediamine the pink colour turned gradually deeper whilst the suspension prepared with an alcoholic solution of diphenylamine at low pH values showed a light green colour. The hydrogen montmorillonite did not contain as exchangeable or adsorbed cations either ferrous nor ferric iron, thus it can be stated that in the bringing about of reactions with benzidine or orthotolidine iron plays no part. An example of such a case was a soil sample from the vicinity of Szeged which contained large amounts of iron hydroxide which produced with benzidine a blue and with orthotolidine a green colour independently from the fact that the curve based on the differential thermal analysis did not indicate the presence of montmorillonite. Therefore, in the presence of larger amounts of limonite the staining method cannot be used.

In the course of the investigations the question arose whether or not the presence of cations, e. g. Na, K, Mg and Ca which are adsorbed, or owing to a cation exchange — perhaps in the ionic state — are present as non-silicate bounds influence the development of the produced colour reaction. The experiments proved that if these cations were combined in a soluble — hence ionic — state with an aqueous solution of benzidine or of any other reagent a colour reaction could not be observed at any pH value. If the following salts: sodium sulphate, sodium perborate, sodium peroxide, potassium chloride, magnesium chloride were

introduced into a hydrogen montmorillonite suspension as essential change did not occur, at the most the running down of the colour reaction was accelerated or delayed which is, however, comprehensible considering that these reactions are oxidation reduction processes producing the colouration. Hence, the exchangeable and adsorptive cations — with the exception of ferric ion in an adsorptive ionic state and possibly Mn — play no part in the production of the colour reaction.

Of course, the pH value of the hydrogen montmorillonites depends upon the introduced substances and changes accordingly. In the case of hydrogen montmorillonites as in that of pure hydrogen montmorillonite the change of the colour due to the reaction depending upon the pH values occurred in the same way as in the case of normal bentonites. This also proves that colour staining is an oxidation phenomenon which is not so closely connected with the lattice as was previously believed.

I had already referred to the fact that benzidine, orthotolidine etc. exhibit different colours in water than in alcohol. Thus it seemed necessary to examine in several solvents in the presence of montmorillonites the behaviour of the organic substances used in the course of our investigations.

Benzidine, orthotolidine, diphenylamine, orthoparapenylene-diamine were dissolved in the following solvents: benzene, hexane, carbon-tetrachloride, ethylether, ethylalcohol and water. The solvents were grouped according to the increasing series of the dipolmoments. If this value was 0 like in the case of benzene, hexane or carbontetrachloride the number of the unbound electrons was also taken into account. It was established that whatever the character of the adsorptivum, if the value of the dipolmoment of the solvent was 0 on using montmorillonite adsorbents no difference in colouration could be observed. If solvents having a dipolmoment were applied the various organic dye stuffs behaved in a different manner. Benzidine and orthotolidine are related reagents with a basic character the only difference between them consists of two  $\text{CH}_3$  groups. Both have a symmetrical structure. It could not be observed that with an increase of the dipolmoment of the solvent the change of the colour was proportional as in ethylether or in water the adsorbent showed an almost similar colour, whereas on using ethylalcohol, representing a middle value, a colour of longer wave length was produced. At the same time di-paraphenylamine in which a NH group links two benzene rings — independently of the solvent — always produced the same colouration with montmorillonite, at the most very slight difference in the colour intensity could be observed. Only in the case of paraphenylenediamine a certain regularity could be established, inasmuch as with the increasing of the dipolmoment colours with shorter wave length appeared. Hence the assumption that when different solvents are used the change of the colour should merely be attributed to the dipolmoment of the solvent is not correct.

Probably in this case a complex process takes place as with such first rate adsorbents like montmorillonite not only the adsorption of the dissolved substances, but also that of the solvent must be taken into



consideration. Furthermore, the dissolved substance which causes the colour reaction can be linked partly directly, and partly indirectly, via the solvent to the adsorbent, in this case to montmorillonite. However, the dipole moment of the solvents may also play such a role that the greater the dipole moment the thicker the liosphere formed if liophil substances are involved, which also influences the deepness of the colour.

#### SUMMARY

At the determination of montmorillonites based on colour reactions the method can be improved if the pH value is controlled. Hence the change of colour of montmorillonite suspensions prepared with aqueous or alcoholic solutions of benzidine, orthotoluidine, diphenylamine, ortho- and paraphenylenediamine could be plotted depending upon the change of the pH on a diagram.

On using different solvents the colour produced by the reaction can change, however, a regularity could not be established. In general the solvents without dipole moments showed an identical colour.

The exchangeable cations — except if  $\text{Fe}^{+++}$  or  $\text{MnO}_2$  are present in larger amounts in an ionic state — play no part in the production of the colour reaction considering that hydrogen montmorillonites also exhibit a characteristic colouration, although in their case all exchangeable cations are substituted by hydrogen.

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