

# DYE ADSORPTION AS A METHOD OF IDENTIFYING CLAYS

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## ABSTRACT

Dyestuffs and other reagents which exhibit characteristic colors when adsorbed on clay granules frequently have been employed as aids in clay identification. The colors generally are believed to result from pleochroic effects and acid-base or oxidation-reduction reaction mechanisms. Certain aniline dyes, solutions of which vary in color according to their hydrogen ion content, may be used to indicate the relative acidity of clay surfaces as well as to heighten the natural pleochroism of kaolin minerals. When a clay sample has been pretreated with acid, the colors assumed by the adsorbed dye depend on the characteristic base exchange capacities of the various clay mineral groups present.

Aromatic diamines, amino phenols, and other compounds which can be oxidized to colored semiquinone cations permit particularly sensitive and positive identification of members of the montmorillonoid family and certain other three-layer clay minerals. Theories concerning the nature of this apparently catalytic oxidation on clay surfaces are inadequate to explain the reactions. New concepts and additional experimental information are needed.

*Introduction.* Staining techniques have been employed effectively in conjunction with petrographic examinations of clay minerals and as accessory tools to more complex methods of analysis. Color tests deserve to be used more widely by clay technologists to complement and supplement the more elaborate methods. They are particularly appropriate as aids to petrographic identification methods because the latter are inapplicable to particles the size of those in most clay samples.

Two factors have operated to discourage wider application of staining tests. The semi-empirical nature of most of these methods has limited their use by workers who have preferred to use only those analytical procedures which are based on widely accepted theory. Others have attempted to employ over-simplified, outdated procedures as universal analytical tests in the field. It is scarcely necessary to add that such efforts frequently have been unsuccessful. When modern techniques are used properly, staining tests can save valuable time in identification work. No one method of clay-mineral analysis, however elaborate, is foolproof; but color tests deserve a place beside the established tools of clay scientists and technologists. The relatively great simplicity and speed which characterize dye staining tests, compared with X-ray diffraction and differential thermal analysis, for example, justify wider application of the color methods. It is the purpose of this paper to review past work and current procedures and to discuss the present state of theoretical knowledge concerning mechanisms of color formation on clay-mineral surfaces.

Mielenz and King (1951) have developed the following criteria as desirable attributes of satisfactory staining tests for clay minerals:

1. Development in particles of clay of colors which are: (a) reproducible, (b) sufficiently characteristic to permit identification of one or more clay mineral species, (c) sufficiently intense to permit ready perception in either reflected or transmitted light, (d) and preferably of hues not common in the minerals themselves
2. Preliminary treatment of samples not sufficiently laborious to make application of the method impractical
3. Interferences sufficiently uncommon as to permit application of the method to the great majority of samples

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4. Conditions favorable to development of characteristic colors easily controlled; for example, not altered critically by moderate changes in ratio between amount of clay mineral and volume of dye solution.

None of the staining procedures described in this paper meets all of the criteria suggested above; but when several tests are combined in a systematic manner, the complete procedure satisfies all requirements.

Staining tests are not capable of identifying unambiguously all of the clay minerals present in many samples of naturally occurring complex mixtures in rocks and soils. The occurrence of interlayered lattices of various clay minerals complicates the problem further. Color tests, nevertheless, provide a wealth of information when applied to a wide variety of samples.

*Standardized Color Descriptions for Staining Tests.* The problem of measurement and standardization of color may be solved by comparing colors observed in staining tests with prepared charts of color chips available in the *Munsell Book of Color*, published in 1942 by Munsell Color Co., Inc., Baltimore, Md. The widely accepted Munsell color system classifies colors according to hue, value, and chroma. The pocket edition, volume I, is adequate for purposes of identifying colors produced on clays by various reagents used in staining tests. This loose leaf booklet contains 20 charts corresponding to each of the 10 hues of maximum chroma and 10 intermediate hues. Each chart is arranged according to value and chroma. For example a color designated as 5.0 PB 3/8 corresponds to the hue purple-blue, a value of 3, and a chroma of 8. Increasing value corresponds to lessening amounts of neutral gray. Increasing chroma corresponds to greater intensity of the given hue. On the charts, value ranges from 2 to 8, and chroma from 2 to 12. The use of a comparison eye piece with the Munsell color charts has been described by Mielenz, King, and Schieltz (1950).

*Staining Tests Dependent on Artificially Induced Pleochroism.* The earliest application of dye staining methods to the identification of clay minerals apparently was made by Grandjean (1909), following the work of Suida (1904) which was applied to numerous other silicate minerals. This early work was concerned with the artificially induced pleochroism of kaolin-group minerals when aniline dyes were adsorbed on their surfaces. Later Ross and Kerr (1931) described the natural pleochroism of kaolinite and mentioned the fact that kaolinite becomes more markedly pleochroic when stained by dyes. In an excellent critical discussion of staining techniques, Faust (1940) described the results of his studies on the artificially induced pleochroism of kaolinite, dickite, and nacrite when treated with crystal violet, methylene blue, malachite green, safranin "O", and basic fuchsin. Faust found that these dyes produced strong artificial pleochroism when applied to the larger crystal aggregates such as books and vermicular forms of kaolinite, whereas dickite crystals stained less readily and nacrite crystals stained very weakly. Both dickite and nacrite exhibited much

less pleochroism. Pleochroic tests are not characteristic of other clay minerals.

Observations of artificially induced pleochroism constitute a necessary step in modern dye staining procedures, but the pleochroic effects are less valuable diagnostic criteria than the characteristic colors which result from the adsorption of aniline dyes and aromatic amines and phenols on clay granules.

*Staining Tests Dependent on Acid-Base Reactions.* Dyestuffs which act as hydrogen-ion indicators in aqueous solutions may be adsorbed on clay-mineral surfaces where the resulting color depends on the availability of hydrogen ions from the clay acid. Such adsorbed dyes may be considered indicators of the hydrogen-ion content of the water film on the clay surface. G. T. Faust's paper (1940) clearly demonstrated the acid-base mechanism of the color reactions of aniline dyes on clay mineral surfaces. Weil-Malherbe and Weiss (1948) discussed at length the differences between color reactions dependent on acid-base mechanisms and those dependent on oxidation-reduction reactions. The recent excellent work of Mielenz and King (1951) indicates that the dyes malachite green, color index No. 657, and safranin "Y," color index No. 841, are the most satisfactory aniline dyes for clay-mineral identification.

Following the suggestion of Merwin (Merwin and Posnjak 1938), Faust used aniline as a solvent for his dye reagents. This was done because aniline penetrated the clay granules better than other solvents and led to more intense characteristic colors. Faust also used nitrobenzene as a dye solvent because it has a stable index of refraction approximating that of quartz; and thus it permits rapid recognition and quantitative determination of the quartz content of a clay-mineral sample. Nitrobenzene has been found to penetrate clay aggregates as well as aniline and does not participate in oxidation-reduction reactions with clays as does aniline. It is characteristic of the acid-base staining reactions that colors develop in the absence of any water other than that present as an adsorbed film on clay samples in the oven-dry condition. Samples should be dried immediately before making the test so that the effective concentration of hydrogen ions in the adsorbed water film may be as high as possible. If this is not done even the hydrogen montmorillonoids may be stained the basic color of the dye. On the other hand, colors are developed by oxidation-reduction reactions only in the presence of bulk water. Another point of difference is the speed with which characteristic colors are developed. In acid-base reactions the colors develop immediately whereas the full development of color by oxidation-reduction mechanisms may take from 5 minutes to a number of hours.

Prior acid treatment of clay samples leads to uniformity in the characteristic colors produced by aniline dyes on different clay minerals. The colors used for identification thus are those developed by hydrogen clays. Since the acidity of clay-mineral surfaces is largely a function of the amount of exchangeable hydrogen, it follows that characteristic colors produced by various clay minerals in acid-base color tests are dependent on the respective base-exchange capacities. These conditions obtain, and the test is characteristic, if the proper concentration of dye solution is used together

with the proper relative amount of clay sample and volume of dye solution. If an excess of dye is used for a given clay sample, the clay granules will be saturated with the basic color of the dye even in the presence of hydrogen montmorillonoids which produce the acid color under proper test conditions. This effect is the result of base exchange, the replacement of hydrogen ions in exchange positions by dye molecules.

The necessity for adjusting the amount of dyestuff added to the sample at hand makes it impractical to attempt to identify very small amounts of montmorillonoids admixed with clay minerals of markedly lower base-exchange capacity. Mielenz and King (1951), however, have been able to identify montmorillonoids in concentrations of as little as 5 percent. Sensitivity of the dye tests for montmorillonoids is also a function of the size of the granules in the sample. The smaller particles of montmorillonoids may be saturated with the basic color of the dyestuff whereas the larger grains are stained with the desired acidic color. Detailed procedures for the use of malachite green and safranin "Y" have been described by Mielenz, King, and Schieltz (1950) and Mielenz and King (1951).

An outstanding advantage of the acid-base tests is that they may be used for semiquantitative determinations of the various minerals present in a clay sample. Using nitrobenzene as a dye solvent, it is possible to identify many mineral constituents with the petrographic microscope. Samples are prepared on microscope slides with cover glasses. The numbers of grains of the various minerals admixed with clays and the numbers of clay granules or aggregates stained each color may be counted to estimate the amounts of the various constituents present.

The acid-base tests employing malachite green and safranin "Y" are the best color tests available for identification of minerals belonging to the kaolin group and probably are applicable to a wider variety of samples than the oxidation-reduction color tests. Hectorite samples, however, are decomposed completely by the necessary acid treatment. The tests are useful for the identification of montmorillonoids if samples contain large amounts of these minerals, but are unsuitable if only small percentages are present. The acid-base dye tests should be used in conjunction with one or more of the oxidation-reduction color tests in order to permit more complete and accurate identification of unknown samples.

*Hendricks and Alexander's Benzidine Test.* In 1940 Hendricks and Alexander (1940) described a qualitative procedure for the identification of members of the montmorillonoid group. The test depended on the adsorption and oxidation of benzidine on clay mineral surfaces. Eisenack (1938) and Hauser and Leggett (1940) independently described clay color changes resulting from oxidation-reduction reactions, but they did not propose to use them as identification methods. Hendricks and Alexander found that any diamines capable of producing colored semiquinone forms on oxidation exhibit the same colors after adsorption and oxidation on montmorillonite surfaces. Semiquinones are "odd electron" compounds, free radicals stable in aqueous solution, which are formed by the loss or addition of one electron at one end of a

system of conjugated double bonds. Semiquinones are stabilized by resonance energy and usually are colored. They are stable only in restricted ranges of pH. Semiquinone cations result from one-electron oxidation of various aromatic diamines, phenols, and certain other organic compounds. The chemistry of semiquinones has been discussed in detail by Michaelis (1935).

Hendricks and Alexander believed their test was the result of fortuitous oxidation of a very small amount of diamine to the semiquinone form on a montmorillonite surface. They found that ferric iron salts and organic matter were capable of producing the blue color in the absence of montmorillonoids. They also found that manganese dioxide was a strong enough oxidizing agent to cause color formation. The inorganic interferences could be removed by prior treatment with hydrochloric acid and the organic matter by peroxides. Reducing agents such as ferrous iron salts and stannous chloride were found to inhibit formation of the blue color. In addition to the presence of an oxidizing agent, it was necessary that the reagent be adsorbed, presumably on montmorillonoid 001 lattice planes. Hendricks and Alexander found prior adsorption of large molecules such as codeine or brucine on montmorillonite samples prevented formation of the blue color. The benzidine test has been the target of much criticism as a result of its indefinite nature (Endell et al., 1941; Krüger and Oberlies 1943; Page 1941; Siegl 1945). Experience with the test has shown that positive tests for montmorillonoids can be obtained with clay samples known to contain none; and, conversely, negative tests have been obtained with known montmorillonite samples.

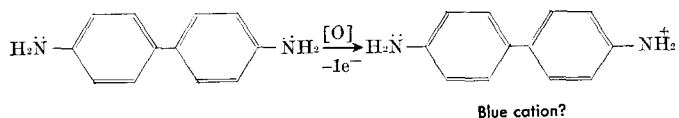
Difficulties encountered in application of the benzidine test to unknown samples probably result from the apparently low oxidation potential of benzidine in neutral aqueous solution and from anomalous adsorption effects. Many relatively weak oxidizing agents are capable of removing one electron from benzidine in neutral aqueous solutions. The presence of such substances in non-montmorillonoid clays would result in false positive tests.

Endell, Zorn, and Hofmann (1941) thought that members of the montmorillonoid group containing large amounts of magnesium or aluminum do not produce blue colors with benzidine, or produce only very weak colors. In agreement with their findings, the writer and others (Mielenz and King 1951) have found that pure hectorite samples produce little or no blue color when treated with benzidine. On the other hand, certain pure, typical montmorillonite samples such as API 11 and 30 from Santa Rita, New Mexico, and API 24 from Otay, California (Kerr et al. 1949), also give weak or negative benzidine tests. Kerr, Kulp, and Hamilton (1949) calculated, according to the method of Ross and Hendricks (1945), the amount of aluminum in tetrahedral co-ordination for 10 of the API collection of montmorillonoid samples. The above-named montmorillonite samples which give very weak or negative benzidine tests, API 11, 24, and 30, and hectorite, API 34a, were found to contain essentially no aluminum substituted for silicon in the tetrahedral layers. This suggests that oxidation of benzidine to the semiquinone form in neutral solution can occur on 001 lattice planes of montmorillonoid minerals only at

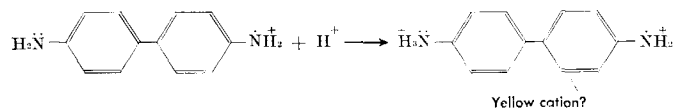
those active spots where silicon has been replaced by aluminum.

*Mielenz and King's Modified Benzidine Test.* Recently Mielenz and King (1951) have suggested an improved modification of the benzidine test which they have effected by adjusting the pH of the reagent solution in contact with a clay sample to approximately one. With montmorillonoid clays, this results in a lemon-yellow particle color rather than the purple-blue obtained in neutral solution. The yellow colors also are stable upon drying. This permits mounting the dried granules on a microscope slide in immersion oil for semi-quantitative determinations in the same manner as the acid-base tests. The newer benzidine test is much more reliable than the older one. It gives positive tests with known montmorillonoid samples and negative tests with samples known not to contain members of the montmorillonoid group.

A tentative reaction equation has been proposed by Weiss (1938) to describe the course of oxidation of benzidine to its semiquinone.



It would be of interest to determine if a different cationic, yellow semiquinone is stable in acid solution at a pH of about 1 such that:



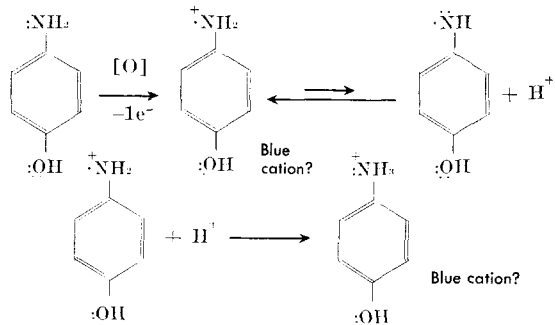
Identification of the blue- and yellow-colored substances necessarily is tentative. Clarification of the nature of benzidine semiquinones stable in various pH ranges awaits precise potentiometric studies.

In addition to identification of montmorillonoid minerals, Mielenz and King have found, empirically, that their modified benzidine procedure permits differentiation of kaolinite from anauxite. Anauxite is stained yellow whereas kaolinite is not affected. This is useful in conjunction with acid-base dye tests.

*Hambleton and Dodd's Para-Amino Phenol Test.* In 1951 Hambleton and Dodd (1953) described the use of *p*-amino phenol as a reagent for the identification of clay minerals by an oxidation-reduction mechanism. Test procedures were developed using various concentrations of alcoholic solutions of the *p*-amino phenol reagent, followed by drying of the alcohol solvent, treatment of the sample with 1:1 hydrochloric acid, and observation of the sample wet and after drying. Reflected light was most satisfactory. White porcelain spot plates, a stereoscopic microscope, and a reproducible intense light source were the only equipment items needed. Characteristic colors were obtained only in the presence of a highly acidic solution. Another test procedure using a saturated aqueous solution of the *p*-amino phenol reagent in a manner similar to the newer benzidine test of Mielenz and King was tried, but it was less successful.

The new *p*-amino phenol test is most sensitive and accurate for the montmorillonoids and the hydrous mica

minerals. It is less satisfactory for members of the kaolin group when these occur in mixtures with other clays. The test is particularly sensitive to relatively small concentrations of montmorillonite or members of the montmorillonoid group in mixtures of clay minerals. Tentative equations for the oxidation of *p*-amino phenol to semiquinone forms are written below:



The *p*-amino phenol reagent is not oxidized to characteristic blue colors by ferric iron or extraneous organic matter, although there is some evidence that the presence of manganese dioxide will give anomalous tests when present in clay-mineral samples. The new reagent appears to have a higher oxidation potential in acid solution than does benzidine in neutral solution.

The most sensitive montmorillonoid test is obtained by use of a 0.1 percent alcoholic solution of *p*-amino phenol as a test reagent. A drop of this solution is applied to about 3 to 5 cubic millimeters bulk volume of clay sample in a depression of a white porcelain spot plate, and the sample is stirred with a toothpick. After evaporation of the alcohol solvent, the dried grains are mixed with a thin glass stirring rod; and one drop of 1:1 hydrochloric acid is added. After 10 or 15 minutes the color of the wet sample is observed. Members of the montmorillonite family are identified by the presence of a characteristic dark blue edging around clay granules or aggregates.

If 0.5 percent and 2 percent reagent solutions are applied to separate portions and the same procedure is followed, it is found that hydrous micas are colored characteristic murky greens, olive greens, browns, yellow greens, or tans on the surface of the main mass of the clay sample. This test often is definitive for the almost invariably impure hydrous micas, but it should be confirmed by acid-base tests.

If 4 percent or 2 percent solutions of the *p*-amino phenol reagent are used in these tests and the samples are allowed to dry following application of 1:1 hydrochloric acid, it is found that blue or purple-blue colors are characteristic of montmorillonoids and that various shades of pink are characteristic of members of the kaolin group unless the latter are present in relatively small amounts. When samples are stained with saturated aqueous solutions of the *p*-amino phenol reagent less satisfactory differentiations are possible, although clay granules may be colored more intensely.

One advantage of the *p*-amino phenol color tests is that they generally may be applied without any previous chemical preparation of the sample. The best procedure is to pretreat unknown samples with dilute hydrochloric acid to remove excess ferric salts and anomalous oxidizing

agents such as manganese dioxide. When the unknown sample contains hectorite or one of the nontronites, the usual pretreatment with 1:1 hydrochloric acid will decompose hectorite rapidly and nontronites slowly. For this reason it is advisable to test for the presence of montmorillonoids before making any routine pretreatment with acid. The time required to examine the sample for the presence of montmorillonite minerals using a 0.1 percent solution of *p*-amino phenol is so short after the addition of the hydrochloric acid, only about 10 minutes, that neither hectorites nor nontronites decompose before a characteristic montmorillonoid test has been observed.

It seems reasonable to assume that color intensities observed in oxidation-reduction staining tests are a function of the relative densities of adsorbed colored semiquinone cations. With mixed-layer minerals in which only a fraction of the total area of 001 lattice planes resembles montmorillonoid crystal surfaces, less intense colors would be expected. The stain would not penetrate those 001 surfaces bonded by potassium ions as in the micas. In the case of relatively pure illite samples, there would be no intervening 001 planes which the stain could penetrate between exterior surfaces. Although these exterior surfaces might resemble montmorillonoid planes, they would constitute only a small percentage of the total 001 planes. Thus there would not be enough of the colored semiquinone cations adsorbed to produce an over-all color effect similar to that observed in the presence of montmorillonoid minerals. The result would be an opaque color which would be a mixture of the semiquinone color and the body color of the sample. By noting these variations in color, it should be possible to identify illite samples by empirically determining the colors produced with known illites after the removal of extraneous coloring material such as ferric salts. This has been done in the development of the *p*-amino phenol procedures. Although not detectable by X-ray diffraction, some penetration of 001 montmorillonoid planes by adsorbed reagents probably occurs.

*Nature of the Oxidizing Agents on Clay Mineral Surfaces.* Hendricks and Alexander (1940) and Weil-Malherbe and Weiss (1948) have assumed that the oxidizing agent responsible for the one-electron oxidation of benzidine to its blue semiquinone on montmorillonite surfaces is lattice-bound ferric iron. Other oxidizing agents probably contribute to formation of the blue benzidine color also. On the other hand, reagent solutions of *p*-amino phenol are not oxidized by ferric ions in acid solution, and montmorillonoid clay-mineral samples which contain essentially no iron cause formation of the blue semiquinone color when treated with *p*-amino phenol and hydrochloric acid. One or more oxidizing agents other than ferric iron must be responsible for semiquinone formation by *p*-amino phenol, and these same agents probably play a role in the oxidation of benzidine.

The empirical nature of oxidation-reduction color tests is in part the result of ignorance concerning oxidation mechanisms which can account for the characteristic formation of colored semiquinone cations only on montmorillonoid minerals. Experimental results suggest there must be a particular kind of oxidant associated with the silicon tetrahedral layers of montmorillonoids, but not

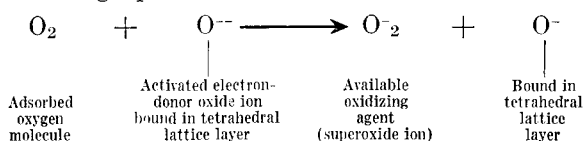
with those of the kaolin minerals, pyrophyllite, or talc. The most outstanding structural differences between these minerals result from isomorphous substitutions in the montmorillonoids of aluminum for silicon in the tetrahedral layers and of magnesium and other divalent cations for aluminum in the octahedral layer. These substitutions are the cause of the inherent electrical charge on the three-layer clay minerals which results in their capacity to adsorb cations on 001 lattice planes. When silicon is replaced by aluminum in the tetrahedral layer, there is an excess of electrons associated with the oxygen tetrahedron surrounding the aluminum ion. When magnesium is substituted for aluminum in the octahedral layer, the resulting electron excess is distributed more diffusely in oxygen tetrahedra on each side of the substituted site. In each case active spots probably are formed on 001 lattice planes. Oxide ions associated with these spots are potential donors of electrons. Exchangeable cations are adsorbed over these sites; non-exchangeable potassium ions are embedded within the open oxygen hexagons adjacent to the activated tetrahedra. Large cations such as the semiquinones of benzidine or *p*-amino phenol must be adsorbed and held by both ionic and van der Waals forces over one or more active spots.

Recently W. A. Weyl (1949) has postulated that the surfaces of clays and finely divided silica exert a

“... strongly oxidizing effect which is comparable with that of ozone. This effect is very strong for the dust of freshly ground quartz, silica gel, clay, and for some other silicates and persists even in the presence of moisture. The oxidizing effect of SiO<sub>2</sub> is enhanced by light, elevated temperature and is proportional to the surface. The quantity of oxygen available is small and its detection requires sensitive methods. The oxidation potential, however, is very high, as can be seen from the fact that silver is oxidized to its peroxide.”

Weyl attributed the specific toxicity of silica and clay dust in the lungs, that is, silicosis, to this powerful oxidizing effect, and thus explained the effectiveness of reducing agents such as aluminum metal dust in therapeutic treatment. Weyl claimed that a specific reagent, 4, 4', 4''-hexamethyl triamino triphenyl methane, indicated the presence of “atomic oxygen” on silica gel at room temperature and on finely divided silica or clay at 150° C. Hauser, Le Beau, and Pevear (1951) have proposed that the release of atomic oxygen on clay surfaces is responsible for oxidation-reduction color reactions. Weyl<sup>1</sup> considers that all oxide surfaces undergo O<sub>2</sub>—O<sub>2</sub><sup>-</sup> ion exchange, one step of which is a one-electron transfer to a chemisorbed oxygen molecule.

In the absence of any more plausible theory, the writer proposes a tentative hypothesis based on the assumption that activated oxygen ions in montmorillonoid 001 lattice planes are capable of transferring an electron to adjacent adsorbed oxygen atoms to form superoxide or perhydroxyl ions, O<sub>2</sub><sup>-</sup>. This reaction might be represented by the following equation:



<sup>1</sup> Personal communication, August 13, 1951.

The concentration of superoxide ion oxidizing agent on 001 montmorillonoid planes would be greater if the electron excess resulted from substitution of aluminum for silicon in tetrahedral layers. Thus, in neutral solution it appears that the effective oxidation potential would be too low to oxidize benzidine to its blue semiquinone cation unless there were such tetrahedral layer substitution. If the montmorillonoid sample contained no aluminum in the tetrahedral layer, the oxidation potential in neutral solution apparently would be lower than that of the ferric-ferrous ion couple.

In acid solution, however, the oxidation potential of superoxide ion would be distinctly higher; and this greater potential would be capable of oxidizing benzidine to its yellow semiquinone and *p*-amino phenol to its blue semiquinone. It is necessary, also, to assume that the blue semiquinone form of benzidine is stable only in neutral and basic solutions, whereas its yellow form and the blue semiquinone of *p*-amino phenol are stable only in acid solution. In acidic solution the oxidation potential apparently is sufficient to cause semiquinone formation even when the positive charge deficiency arises from octahedral layer substitution. Thus hectorite produces semiquinone colors in acid systems (before decomposition) but not in neutral solutions.

It is possible that other reagents besides benzidine and *p*-amino phenol may be found suitable for oxidation-reduction color tests. The selection of these two reagents is based on the empirical observation that their semiquinones are sufficiently stable in a pH range which may be utilized in test procedures. Apparently the blue semiquinone of *p*-amino phenol is stable only in a much more acid medium than the yellow benzidine semiquinone.

*Color Test Procedures.* Mielenz and King (1951) have developed a standard procedure for the identification of clay minerals by staining tests. They employ characteristic differences in birefringence to differentiate between the two- and three-layer clay minerals, followed by observation of the colors produced by malachite green and safranin “Y” dye solutions. In this manner they detect divisions in the kaolin group, that is, kaolinite and anauxite, dickite and nacrite, and the halloysites. Pleochroic effects aid in distinguishing kaolinite and anauxite from dickite and nacrite. The acid benzidine test may be used (with a different sample) to differentiate kaolinite and anauxite.

Montmorillonoids are recognized if present in amounts greater than 5 to 10 percent, and glauconite and celadonite fail to stain sufficiently to mask their yellow or greenish-yellow body colors. The acid benzidine test then may be applied to distinguish small percentages of montmorillonoids. Experience is necessary to distinguish between illites, vermiculites, and palygorskite or attapulgite. In place of the acid benzidine test at this stage of the analysis, *p*-amino phenol can be used to confirm the presence of montmorillonoids, including hectorite, and to aid in determining the hydrous micas. In addition, *p*-amino phenol is helpful in identifying halloysites by producing characteristic mottled brown granule edges, and it may aid in confirming other members of the kaolin group.

Finally, a word of caution is in order. Before applying staining tests as a new procedure, it is advisable to

observe results obtained with known mineral samples. Experience is indispensable.

*Discussion.* Staining test procedures described in this paper generally are too involved to permit ready adaptation to field identification of unknown samples. Much of the unwillingness to apply staining tests stems from unfortunate experience acquired when the tests were used in the absence of information concerning their limitations. Development of color tests has reached the point today where reliable laboratory analytical procedures can be utilized to save time and expense. Numerous laboratories, such as the Bureau of Reclamation Petrographic Laboratory in Denver, have developed routine procedures which have proved to be most dependable in the hands of properly trained analysts. Difficulties in the use of staining tests have arisen when general "shotgun" applications of one overly simplified procedure have been made to complex unknown clay samples.

Enough development work has been done at this time to permit any clay laboratory to set up generally reliable procedures for the identification of most of the known clay minerals. Many checks and counterchecks have been developed to improve the accuracy of the tests. If the color tests are properly used in conjunction with petrographic and other more complex analytical procedures, they will be found to be a most helpful addition to the tools of the clay technologist.

In addition to wider application to analysis, there is a possibility that color tests, particularly those based on oxidation-reduction reaction mechanisms, will be useful in elucidating differences in structure among the three-layer clay minerals. Less is known concerning the hydrous mica clays than those of the kaolin or montmorillonoid groups. G. Brown (1951) has presented the hydrous micas as a continuous series of minerals between the well-crystallized micas and the expanding montmorillonoids and vermiculites. Mixed-layer minerals were included with other hydrous micas. The use of reagents such as benzidine, *p*-amino phenol, and other similar compounds which can be oxidized to colored, stable semiquinone cations may be used to differentiate between hydrous micas of varying crystallinity and to detect mixed-layer minerals containing various amounts of montmorillonoid or vermiculite layers. Such differentiations might be made by studying the variations in color produced with a given reagent.

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#### DISCUSSION

**J. L. Hall:**

Could differentiation between kaolinite and anauxite by the dye adsorption technique be discussed in more detail?

**M. E. King:**

An aqueous solution of benzidine is added to an acid-treated sample. After the sample is dried, it is acidified with 1:1 HCl and again dried. When such a treated sample is mounted in immersion oils and is viewed under a petrographic microscope and

transmitted light, anauxite is lemon-yellow whereas kaolinite is colorless. This procedure is described in detail in a recent paper by Mielenz and King (1951). The method has been checked on anauxite from the type locality at Bilin, Czechoslovakia, and from the Ione formation of California.

**B. B. Osthaus:**

What method is used to remove iron compounds and organic matter?

**M. E. King:**

A 1:1 solution of water and hydrochloric acid is used to remove iron compounds and a solution of hydrogen peroxide to remove organic matter. However, caution must be used in treatment of samples thought to contain minerals susceptible to breakdown in this concentration of acid.

**R. E. Grim:**

How successful are you in using the dye tests for the identification of clay minerals in samples which are an intimate mixture of various clay minerals? For example, in a mixture of kaolinite, illite, and montmorillonite? What is the sensitivity of the dye test?

**M. E. King:**

A combination of the various dye tests generally enables a satisfactory separation of clay minerals in such a mixture. The main difficulty arises in detection of clay minerals not reacting positively in the tests where they are intimately admixed in a very finely divided condition with clay minerals which react positively. No difficulty is experienced with mixtures if the particles are large enough for easy inspection microscopically. An illustration of the application of staining tests is the differentiation of illite from montmorillonite by the combination of Dodd's test using para-amino phenol with the benzidine test. If a material develops a deep prussian-blue color with para-amino phenol, and shows no change in color after acidification and the addition of a drop of benzidine, then the tests indicate that the material consists of montmorillonite. If the color disappears entirely or changes to a very light pink, then the tests indicate that the material contains illite or hydrous mica.

With the use of malachite-green and safranin "Y," identification of montmorillonite is reliable if montmorillonite constitutes more than 5 percent of the sample, but with the modified benzidine test even one particle of montmorillonite in a mixture can be identified. In general, the dye tests are as sensitive as are any of the other methods.

**Isaac Barshad:**

Did you ever use dye tests to differentiate the different mica minerals or a K<sup>+</sup>-saturated montmorillonite and a K<sup>+</sup>-saturated illite?

**M. E. King:**

Yes, we found that muscovite, biotite, phlogopite, and lepidolite, for example, do not react with any of the dyes regardless of the pH. All of our dye tests are carried out in an acid medium; therefore, even though montmorillonite might be K<sup>+</sup>-saturated to begin with, it becomes H<sup>+</sup>-saturated and reacts with dyes. K<sup>+</sup>-saturated illite, after acidification, causes only a slight change in the color of safranin "Y" or malachite-green. Moreover, when illite treated with benzidine is acidified to pH 1 and subsequently dried, no coloration is evident with transmitted light. Details of these reactions are described by Mielenz and King (1951).

**R. C. Mielenz:**

We have come to feel that the adsorption of dye molecules by clay minerals offers a tool whereby a better understanding of the phenomenon of adsorption may be gained, for upon adsorption of dye molecules not only can one measure the amount adsorbed and the changes in the crystal lattice dimensions, but also the color transformation in the dye indicates some change in the organic molecule itself which may be related in some way to the forces with which it is bonded to the surface.

Regarding the likeness of the montmorillonite and the illite surfaces, it may be true theoretically that these surfaces should be alike; but, since the dye tests indicate that they are not alike, the task before us is to find out what the difference is between them rather than to ignore it.

**V. T. Allen:**

Has anyone had difficulties with the benzidine test on the minerals of the kaolin group? We had several kaolins which by all other tests contained no montmorillonite, but the sample still gave a blue test with benzidine.

**M. E. King:**

I observed the same thing with a kaolinite from Macon, Georgia, but X-ray analysis revealed that the sample contained about 5 percent montmorillonite, thus explaining the anomalous result obtained with the dye test.

In kaolin samples which do not contain any montmorillonite but still give an abnormal color test with benzidine, the abnormality may possibly be associated with the degree of fineness of the mineral grains. A high degree of fineness may indicate the presence of a considerable number of broken bonds which may cause oxidation of the benzidine, but the blue color that results is never as intense as that produced by montmorillonite. Such possible difficulties may be overcome by acidifying the clay sample during the test to a pH of about 1. Upon subsequent drying of the sample, kaolinite will not show any blue or yellow coloration in transmitted light under the petrographic microscope.

**Padraic Partridge:**

Will an increase in surface area of kaolinite, which may result upon grinding, explain some of the abnormal test colors as well as the large increase in the cation-exchange capacity which have been mentioned?

**W. F. Bradley:**

Because of the hemimorphic nature of kaolinite, it is doubtful whether any surfaces should really be called abnormal. Each crystal must of necessity present both an oxygen and a hydroxyl surface in addition to less extensive edges. The large increase in the base-exchange capacity of kaolinite upon grinding, as in the experiment reported by Kelley, is not necessarily due to an increase in surface area. Although an increase in surface area undoubtedly results from grinding, the new surfaces which are exposed would most likely be additional oxygen and hydroxyl surfaces parallel to the 001 plane; and since such surfaces are electrically neutral, the large increase in the base-exchange capacity is due most likely to some other phenomenon which simulates base exchange.

**Isaac Barshad:**

Is it possible that a permutite-like substance is formed from the decomposition products of kaolinite released during grinding? That kaolinite decomposed during grinding was revealed by differential thermal and X-ray analyses. This decomposition is revealed in DTA by a reduction in the magnitude of the endothermic break characteristic of kaolinite and in X-ray analysis by a weakening in the intensities of diffraction lines of the kaolinite pattern. I see no reason to question the possibility of the formation of a permutite-like material of high exchange capacity from the released silica and alumina.

**W. P. Kelley:**

Can permutite be produced from a mixture of silicon dioxide and aluminum oxide with no other elements present except water?

**G. A. Mickelson:**

By bringing together various proportions of tetraethyl orthosilicate and aluminum isopropoxide, C. L. Thomas (1949) produced a whole series of permutite-like substances of varying silica-alumina ratios ranging in exchange capacity from 100 to 600 me. per 100 g. Although there were no cations such as Na<sup>+</sup> and K<sup>+</sup> present, I do not see why aluminum ions, simple or complex, cannot act as exchangeable cations to satisfy the exchange positions due to tetrahedral aluminum ions characteristic of such permutites.

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