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The Acidity of Clay Minerals in Polymerizations and Related Reactions

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SUMMARY

The chemical activity of mineral fillers, under conditions similar to those encountered in filled-polymer systems, has been studied. It is shown that, contrary to previous views, the alumino-silicates have strongly acidic surfaces and that this surface acidity influences the chemical reactions in polymeric composites. Although the number of acid sites is significantly less than those of cracking catalysts, the strength of the sites is of a similar order of magnitude. A study of the infrared spectra of pyridine adsorbed on kaolin has shown that both Lewis and Brønsted acid sites are present. The ratio of Lewis to Brønsted acid sites varies with the free moisture content of the clay.

Neutralization of the clay by amines and various other organic solvents has been investigated. The chain length, basicity, and chain branching of the solvent or additive are important factors to consider when neutralizing the clay for use in practical systems.

INTRODUCTION

The changes in the properties of thermoplastic or thermosetting polymer compositions that result from the incorporation of mineral fillers are generally attributed to the physical characteristics of the filler. With the exception of carbon black and fine particle size silica, fillers are often assumed to have little or no chemical influence on the cross-linking reactions in thermosets or on the subsequent degradation reactions in filled polymer compositions. A number of recent reports [1-3] indicate that clays can promote chemical reactions, particularly under conditions where relatively nonpolar media are being used, and that these chemical effects of the clay fillers can have a significant bearing on the composite properties.

In this paper we attempt to define the nature of the chemical activity associated with clay fillers, in particular, kaolinite, and to indicate the magnitude of the activity. Subsequent papers will relate these parameters to the manner in which kaolinite and similar fillers affect polymerization and related reactions.

DISCUSSION

Two important characteristics that have been noted in reactions catalyzed by clay minerals are, first, that the activity increases as the mineral is dried, and second, that the activity is greatest in nonpolar media.

Most reactions catalyzed by minerals show the general characteristics expected of carbonium ions, and this observation suggests that the clay's activity is related to its acidity. In this discussion the term "acidity" will be used in a broad sense and will include the ability of the mineral to act as a proton donor (Brønsted acid) or as an electron acceptor (Lewis acid).

The kaolinites used commercially in organic polymers are usually specified in terms of their physical characteristics, the pH, and the "free" moisture content as estimated by weight loss at 110°C. The pH is measured in a 20% slurry of kaolin in water and under these conditions kaolin has a pH in the range 4.5-7.

A much more meaningful value of acidity would be that of the clay as used in typical organic media where the "free" moisture content is less than 1%, and is often in the range 0-0.5%. For example, in paint and related systems the clay usually has a moisture content of approximately 1% but in plastics and elastomers, where the polymer-filler mixture reaches temperatures in excess of 100°C during processing, surface moisture is lost and the residual water is likely to be 0 to 0.2%. The pH as measured in

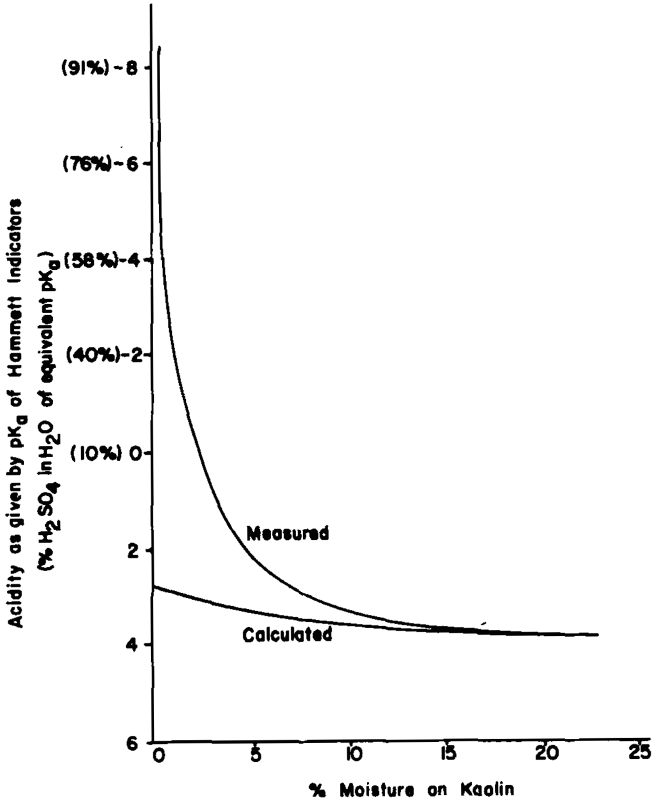

Fig. 1. The relationship between the moisture on kaolin and acidity.

water is quite misleading if used to predict acidity in nonaqueous organic media. This is shown in Fig. 1 where the surface acidity at various moisture contents, has been measured.

Three points of special significance to the present discussion are:

1) The extremely acidic surface of "dry" kaolinite which can have a pK_a of -8.1 and is therefore equivalent in acidity to a solution of 90% sulfuric acid [4].

2) Over the specified limits of water content there is a wide range in acidity. At 1% moisture the $pK_a = -3.0$ (equivalent to 48% H_2SO_4) and at 0% moisture, the $pK_a = -8.1$ (90% H_2SO_4).

3) The "dry" condition referred to is reached under extremely mild conditions and could readily be found in commercial clay samples.

To formulate useful composites and to control the acidity of mineral surfaces, information is required on two factors; the number and the strength of the acid sites. An accepted technique for measuring the number of sites has been developed for silica-alumina cracking catalysts [5], and to place this discussion in perspective with related work on the cracking catalysts it is informative to measure acidities by butylamine titration as described by Benesi [6]. The results show that kaolinite has sites of equivalent strength to those of cracking catalysts but that there are only 1/5th the number (Table 1). Although the number of sites appears to be small, their effect can be significant particularly if chain reactions are involved. Examples of this situation are the polymerization of styrene in unsaturated polyesters [7] and the termination of radical reactions in elastomers [8].

Other alumino-silicates [5] also have acidic surfaces. The strength and number of acid sites depends on the mineral structure, for example, montmorillonite (bentonite) has more sites than kaolin but their acid strength is less than the strongest on kaolin. On the other hand, talc, a

Table 1. The Number and Maximum Acidity of Acid Sites on Dry Minerals

Mineral	pK_a range of strongest sites	Total acidity to pK_a (mequiv amine)
Kaolin	<-8.2	0.04
Montmorillonite	-5.6 to -8.2	>0.2
Attapulgite	<-8.2	>0.2
Talc	4.0 to 3.3	0.005
TiO_2-silica-alumina coated	3.3 to 2.8	0.005
Calgonized kaolin	1.5 to -3.0	0.04
Sodium kaolin	-3.0 to -5.6	0.03
Alumino silicate catalyst	<-8.2	0.20

magnesium silicate, has only a few weak sites (Table 1). TiO_2-silica alumina coated has a similar number of sites to talc but they are slightly more acidic.

The surface acidities were measured in a nonpolar medium (hexane or benzene) but most organic polymers contain polar functional groups or additives. Consequently the effect of the molecular weight of the neutralizing molecule and of the type of functional group on the acidity was investigated. With organic amines the neutralizing power increases slightly with increasing chain length (Fig. 2) or with the area covered by the alkyl moiety (Fig. 3) (tert-butylamine is more effective than n-butylamine). The results suggest that amine groups attached to polymer molecules will be more effective in neutralizing the surface than butylamine. This is consistent with the observations made on cracking catalysts that the acid sites are close together [9]

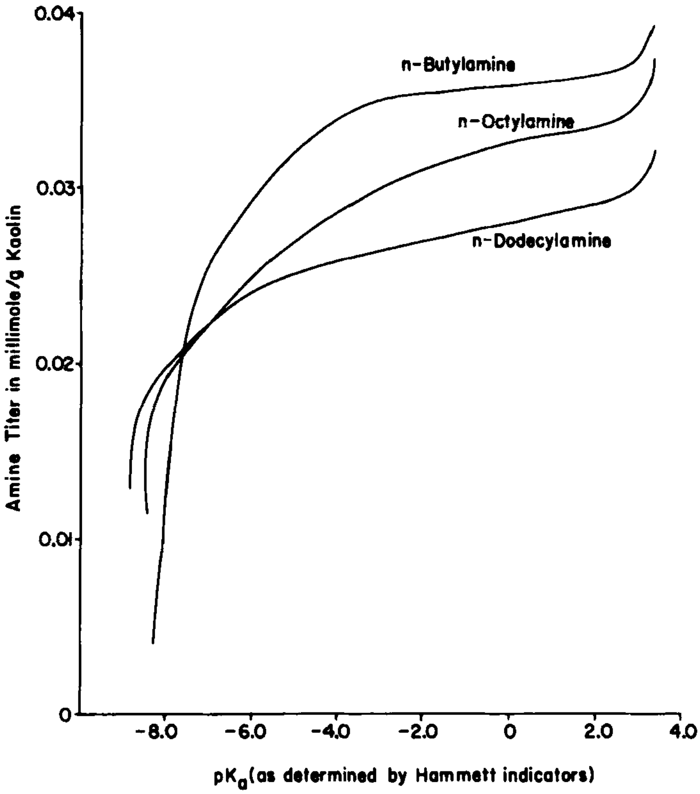

Fig. 2. Kaolin-amine titration curves.

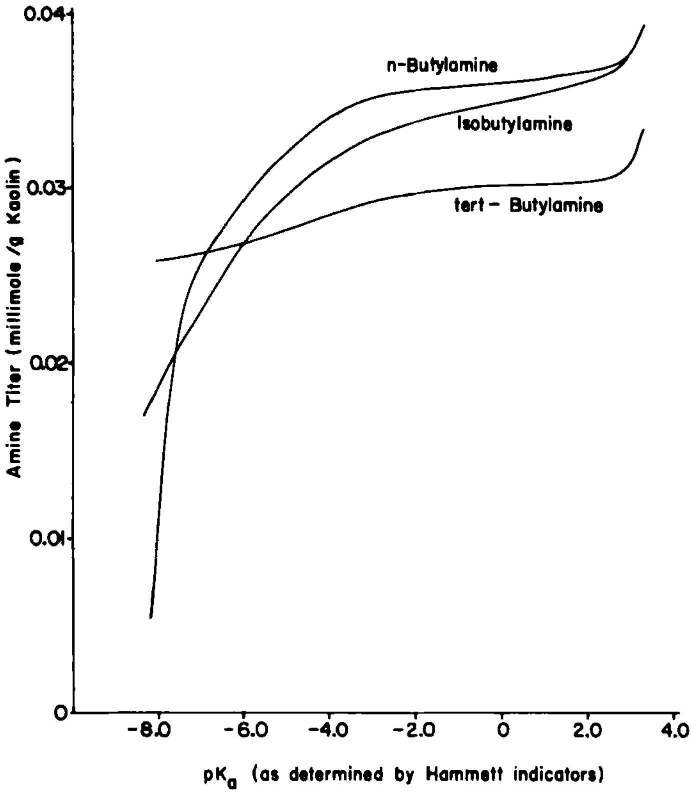

Fig. 3. Kaolin-amine titration curves.

and that the amine group is adsorbed strongly by an acid-base interaction, whereas the alkyl tail "neutralizes" a few sites by steric blocking. Water and short chain alcohols (methanol, ethanol) are much less effective than amines in neutralizing the surface. This is to be expected in view of the weaker basicity of alcohols and water. On an equivalent basis ethanol is only 1/10th as effective as ethylamine in neutralizing the surface to a pK_a of -5.6. Alcohols above C_3 are even less effective (Table 2) which is consistent with the lower basicity shown by longer chain alcohols in other solvents [10]. It is also known that thermodynamic acitivity of alochols in benzene solution decreases with increasing chain length [10a].

The lower apparent basicity shown by the higher alcohols could also result from the attraction of the alkyl tail for the solvent. This attraction is comparable in strength to that of the bonding of the hydroxyl group to the surface.

Table 2. The Effect of Various Alcohols on the Acidity of Dry Kaolin[a]

Alcohol added	pK_a range
Methanol	3.3 to 4.0
Ethanol	3.3 to 4.0
n-Propanol	-3.0 to 1.5
n-Butanol	-3.0 to 1.5
n-Pentanol	-3.0 to 1.5
n-Hexanol	-3.0 to 1.5
n-Octanol	-3.0 to 1.5
n-Decanol	-3.0 to 1.5

[a] Concentration used was 50 mmole/g clay. No other solvent was present.

This is in marked contrast to the amines where strong interactions occur between the functional group and the acidic surface, and these override the relatively weak forces of attraction between the alkyl tail and the solvent.

These observations on the relative ineffectiveness of long chain alcohols for neutralizing surface acidity in kaolinite have immediate practical consequences in unsaturated polyesters. The use of low moisture-content clays is undesirable because they promote the spontaneous cationic polymerization of the styrene and interfere with the free radical reactions involved in the cure of the polyesters [7]. The residual hydroxyl groups at the chain ends of the polyester do not neutralize the dry clay surface sufficiently to prevent these reactions. On the other hand, methanol and water at the same molar concentration are able to reduce the surface acidity, and useful clay/polyester compositions are possible. For example, in filled polyesters the use of a clay with a surface moisture content of 0.3% or less (which corresponds to a pK_a of less than -5.6) led to poor can stability. If the clay contained 1% water or the equivalent amount of methanol, satisfactory stability could be obtained. Other properties were satisfactory.

The effect of other solvents of various polarities on the acidity of clays has been investigated (Table 3). Ketones are similar to alcohols whereas ethers and esters (weaker bases) cause only slight changes in the acidity.

Table 3. Effect of Other Solvents on Acidity of Dry Kaolin[a]

Additive	pK_a range
Acetone	1.5 to 2.8
Methyl ethyl ketone	1.5 to 2.8
Methyl amyl ketone	1.5 to 2.8
Ethyl acetate	-3.0 to -5.6
Amyl acetate	-3.0 to -5.6
Di-n-amyl ether	-3.0 to -5.6
Dioxane	-5.6 to -8.2

[a] Amount used = 50 mmole/g clay. No other solvent was present.

The addition of organic bases to neutralize the acidity has another important feature in that this can produce organophilic clays which may be more easily incorporated into organic polymer systems. The chain length of the base relates to the organophilicity of the treated clay as shown in Figure 4; for clays treated with amines, longer chain lengths give lower viscosity in a hydrocarbon medium. This aspect will be reported on more fully in a later communication.

The surface acidity of kaolin can also be reduced by neutralization with inorganic bases. Some control is also possible by selection of the exchangeable cation.

The results of Mortland [3], Fripiat [11], and others [12] on the influence of exchangeable cations on the acidity of the related aluminum silicate, montmorillonite, have shown that if the cation is small and has a high positive charge, the surface acidity tends to be greater. For example, on drying, calcium montmorillonite becomes more strongly acidic than sodium montmorillonite.

The anion associated with the inorganic treatment influences surface acidity (anions are Lewis bases and would be adsorbed at Lewis acid sites). Sodium hexametaphosphate (Calgon) is particularly effective as the hexametaphosphate anion covers the crystal edge [13], the site of much of the kaolin activity [14]. This difference is clearly shown in the vulcanization of elastomers where the Calgon-treated clays give better cure [8].

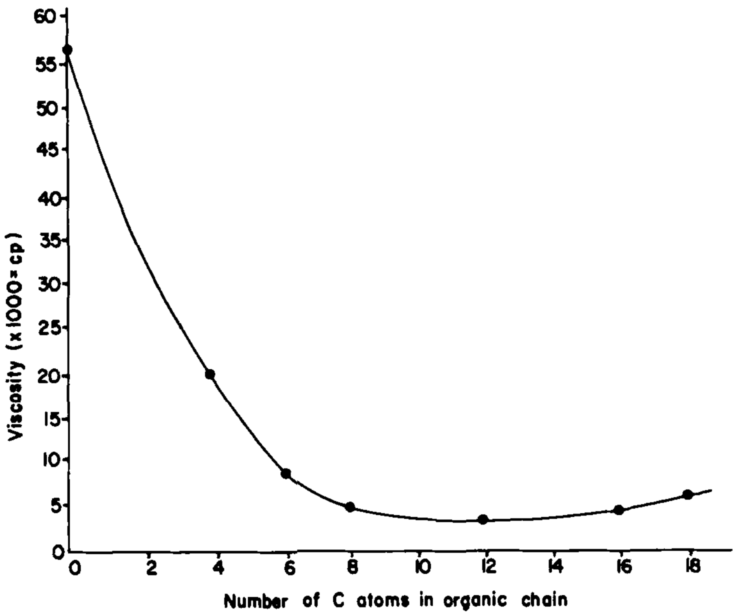

Fig. 4. The relationship between the chain length of the neutralizing amine and viscosity of kaolin in mineral oil.

Calgon-treated kaolins (marketed as predispersed clays) are less acidic than the sodium form prepared by sodium chloride treatment. These results are shown in Table 1.

LEWIS vs. BRØNSTED ACIDITY

Dry clay readily initiates the polymerization of styrene and in discussions on the mechanism of the reaction both Brønsted and Lewis acidity have been invoked. Attempts to correlate Hammett acidity and the influence of various polar groups on the clay/styrene reaction (Table 4) fail if only Brønsted acid sites are invoked and consequently direct evidence for the presence of Lewis sites was sought. Pyridine is useful for this purpose because the IR adsorptions of pyridinium and coordinated pyridine are sufficiently different to allow distinction between the types of acidity [15].

The IR spectra of pyridine adsorbed on clays of various water content show that clay with 1% free moisture behaves only as a Brønsted acid whereas "dry" clay exhibits some Lewis character. The presence of Lewis sites is supported by the conversion of leuco dyes to the corresponding dyestuff with dry clay. Pines and Haag [16] claim that these reactions are specific for Lewis acid centers.

Clay which will initiate the polymerization of styrene contains Lewis acid sites but it is difficult to unequivocally assign the catalytic activity to these sites. A possible explanation is that they activate the adjacent Brønsted sites. This activation of Brønsted sites by adjacent Lewis sites has been reported for silica-aluminum cracking catalysts [9].

Table 4. The Effect of Bases on the Kaolin-Initiated Polymerization of Styrene (base added to give a $pK_a = -5.6$)

Base	Styrene polymerization
Water	Polymer formed
Ethylamine	No polymer
n-Butylamine	No polymer
Methanol	No polymer
Ethanol	No polymer
Butanol	No polymer
Polyester	Polymer formed
Methyl ethyl ketone	No polymer
Methyl amyl ketone	No polymer
Ethyl acetate	No polymer
Amyl acetate	No polymer
Di-n-amyl ether	No polymer
Dioxane	No polymer

Structural Characteristics of Kaolinite Responsible for Acidity

Kaolinite has a layer silicate structure comprised of a silicon-oxygen tetrahedral sheet in conjunction with an octahedral sheet which contains aluminum. These sheetlike structures are stacked one on top of the other to give a layer structure. As a result of isomorphous substitution of either the silicon or aluminum, kaolin has a net negative charge which is balanced by cations (often called exchangeable cations) located on the surface.

The reasons for the increase in acidity as the mineral is dried are discussed elsewhere [17] and can be summarized as follows: First, the removal of water exposes aluminum atoms located at edge sites; this creates possible Lewis acid centers. Second, as the water content of the clay drops below that required to saturate the solvation shells of the exchangeable cations, the residual water dissociates more readily and hence is more acidic. This gives rise to Brønsted acidity. Third, structural changes occur within the silicate lattice and these give rise to both Brønsted and Lewis acidity.

It is suggested that alcohols neutralize the surface in a manner similar to water by occupying the vacancies, produced on drying, in the solvation shells and in the silicate structure. To neutralize the surface in this manner, more than one molecule of alcohol per acid site may be required.

Amines act as simple bases by accepting protons from Brønsted sites or by donating electron pairs to Lewis sites.

CONCLUSIONS

Under the conditions in which clay fillers are used in organic polymers, the surface is strongly acidic and comparable in acid strength to that of cracking catalysts. However, the number of sites is much less than is found with cracking catalyst.

Brønsted acidity predominates on the clays as supplied (moisture content 0.5-1%) but at lower moisture levels, such as those expected during hot milling, some of the acid sites change in character. They become much stronger and show Lewis-type characteristics.

The surface acidity may profoundly affect the chemical reactions in polymer compounds and the effects are particularly noticeable in nonpolar media. Some reactions related to surface acidity are the polymerization of styrene, the decolorization of DPPH [18], and the heterolytic breakdown of organic peroxides [19].

EXPERIMENTAL AND RESULTS

Materials

The mineral was ground to give a particle size of approximately 2 μ. Polyphosphate-modified minerals were prepared by the method of Solomon et al. [8]. Homionic minerals were prepared by treating the mineral with ion exchange resins or by treatment with 1 N NaCl solution.

All solvents and amines were AR quality which were further purified and thoroughly dried by standard methods. The indicators were those described by Benesi [20] and were recrystallized to have melting points corresponding to those reported in the literature. Leuco crystal violet, malachite green, and tetramethyl base were recrystallized and had melting points corresponding to those reported in the literature.

Titration Procedure

The titration procedure was similar to that used by Benesi [6] except that the sample (1.000 g undried) was placed in small screwcap bottles and then heated at 110°C for 2 hr. The bottles were then removed from the oven, immediately capped, and placed in a desiccator until cooled to room temperature. After addition of a solution of the amine in benzene and equilibration for 1 hr (longer times of equilibration made no difference to the results), the samples were tested with indicators. To a similarly treated sample, styrene (1 ml) was added. This solution was tested for polystyrene by addition of a few drops to methanol after 5 and 30 min. Figures 2 and 3 show the effect of chain length and chain branching, respectively, on the plot of titer of amine vs. acid strength of kaolin.

Titration of the kaolin with solutions of methanol, ethanol, and n-butanol in benzene was carried out in a similar manner. The effect of water was determined by saturating the clay with water and then partially drying the clay. The results with alcohols and water are shown in Fig. 5.

Acetone, methyl ethyl ketone, dioxane, and ethyl acetate in benzene were also added to dry kaolin. The pK_a and the ability of the kaolin-solvent system to polymerize styrene were measured.

The results of indicator tests are shown in Table 2 and 3, and those for styrene, including those in the presence of amines and alcohols, in Table 4.

Pyridine-Clay Reaction

The IR spectra of pyridine adsorbed on clay were measured on a Perkin-Elmer 521 Grating Infrared Spectrophotometer. With only a relatively small number of acid sites on clay, it is difficult experimentally to obtain good IR spectra, so that in some cases changes in the spectra rather than absolute band assignments were used. This approach has been recommended by Bourne et al. [15]. Undried kaolin was added to pyridine and allowed to stand for 1 hr. Excess pyridine was pumped off (0.5 mm at

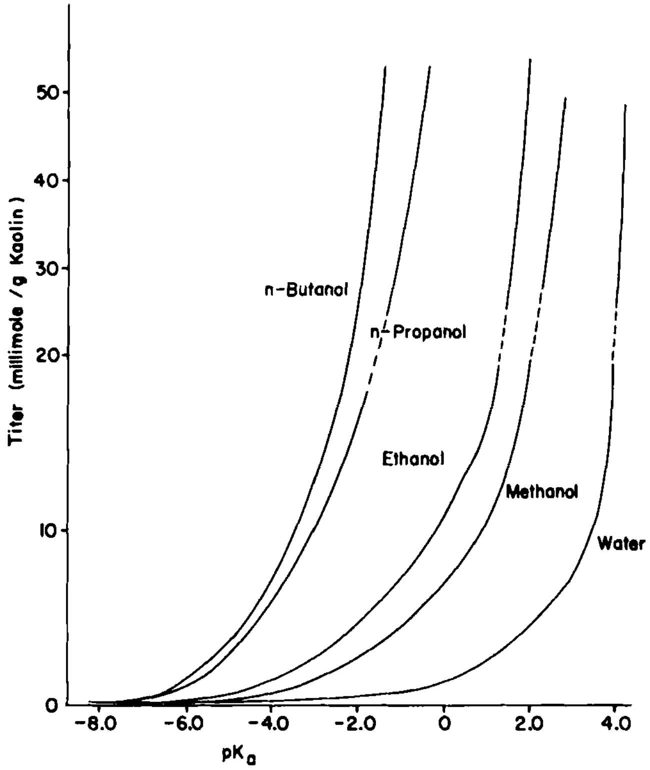

Fig. 5. Kaolin-alcohol/water titration curves.

20°C) and then the sample run as a halocarbon mull. A sample of dry clay was also treated with pyridine, taking care that all moisture was excluded, and the mixture was heated in a sealed tube in an oil-bath (130°C) for ½ hr. Excess pyridine was pumped off (0.5 mm at 20°C) and the IR spectra run as a halocarbon mull between NaCl disks. All operations were carried out in a dry box. The mull was then exposed to a moist atmosphere and the IR spectra run again. Undried clay gave a band at 1540 cm^{-1} which also appeared to a lesser extent in the dry clay. This band increased on exposure of the clay to moisture and is indicative of pyridinium adsorption [15]. The 1480 cm^{-1} band usually found in pyridine moved to 1490 cm^{-1} which is also indicative of pyridinium being present. With dry kaolin, bands at 1456 and 1498 cm^{-1} were observed which correspond to firmly held Lewis pyridine [15]. Any bands due to pyridine adsorption in the region 1610 and 1650 cm^{-1} are obscured by the clay absorbance.

Reaction with Leuco Bases

The leuco dyes were dissolved in benzene and reacted with dry clay in the absence of air. The color of the corresponding dyestuff developed and these compounds were characterized by visible spectroscopy using a Beckman DK-2 Ratio Recording Spectrophotometer.

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REFERENCES

[1] D. H. Solomon, *Clays and Clay Minerals,* **16**, 31 (1968).

[2] H. Z. Friedlander, *J. Polym. Sci., Part C,* **4**, 1291 (1963).

[3] M. M. Mortland, *Trans. 9th Int. Cong. Soil Sci., Adelaide,* **1**, 691 (1968).

[4] L. P. Hammett and A. J. Derup, *J. Amer. Chem. Soc.,* **54**, 2721 (1932).

[5] Z. G. Zul'fugarov, A. A. Bakhshi-zade, L. Sh. Zul'fugarov, N. A. Smirnova, and I. I. Pis'man, *Kinet. Catal.,* (Eng. Transl.), **10**(4), Part 2, 749 (1969).

[6] H. A. Benesi, *J. Phys. Chem.,* **61**, 970 (1957).

[7] D. H. Solomon, *Aust. Oil Colour Chemists' Assoc. Proc. News,* **5**(3), 4, (1968).

[8] D. H. Solomon and J. D. Swift, *J. Appl. Polym. Sci.,* **11**, 2567, (1967).

[9] L. A. Ignat'eva and G. D. Chukin, *Doklady Phys. Chem.* (English Transl.) **184**, 66 (1969).

[10] C. R. Noller, *Chemistry of Organic Compounds,* Saunders, London, 1965, p. 986.

[10a] I. Brown, W. Fock, and F. Smith, *J. Chem. Thermo.,* **1**, 273 (1969).

[11] J. J. Fripiat, *Clays and Clay Minerals,* Proc. 12th Nat. Conf., 327 (1964).

[12] J. D. Russell, M. I. Cruz, and J. L. White, *J. Agr. Food Chem.,* **16**(1), 21 (1968).

[13] H. Van Olphen, *An Introduction to Clay Colloid Chemistry,* Wiley, New York, 1963, p. 112.

[14] D. H. Solomon and M. J. Rosser, *J. Appl. Polym. Sci.,* **9**, 1261 (1965).

[15] K. H. Bourne, F. R. Cannings, and R. C. Pitkethly, *J. Phys. Chem.*, 74, 2197, (1970).
[16] H. Pines and W. O. Haag, *J. Amer. Chem. Soc.*, 82, 2471 (1960).
[17] D. H. Solomon, D. G. Hawthorne, and Jean D. Swift, *J. Catal.*, In Press.
[18] D. H. Solomon and D. G. Hawthorne, *J. Macromol. Sci.–Chem.*, **A5**, 573 (1971).
[19] D. H. Solomon, J. D. Swift, and I. G. Treeby, *J. Macromol. Sci.–Chem.*, In Press.
[20] H. A. Benesi, *J. Amer. Chem. Soc.*, 78, 5490 (1956).

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