

PERSPECTIVES IN APPLIED ORGANO-CLAY CHEMISTRY¹

by

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ABSTRACT

Some aspects of organo-clay chemistry that have interested a growing number of scientists are reviewed and discussed. Particular attention is directed to published evidence for the "reality" of clay compounds, the possible effects of high energy radiation on clay properties, industrial applications of modified clays and the increasing number of patents being granted in this field of applied chemistry. A number of areas of inadequate information where further basic research could lead to useful applications is pointed out.

INTRODUCTION

In a bird's eye view of applied organo-clay chemistry, I can hardly do more than offer what might be considered an expanded outline for a book. The interest in this special area of clay chemistry has increased so greatly in the last decade that to keep up with the literature is almost a full-time job. In this respect, however, we have been helped greatly in the past by such books as those of Hauser (1955, pp. 122-138, 155-180) and Iler (1955a, pp. 220-232) and, particularly, Grim (1953, pp. 250-277) which contains the most comprehensive survey of the clay-organic literature through about 1951. To cover the next period up to the Ninth Clay Conference (1960) we have the annual *Clays and Clay Minerals Proceedings*. The subject has grown to such an extent that all-day "Symposia on Clay-Organic Complexes" were held at both the Ninth and Tenth Clay Conferences. In giving the keynote address at the Ninth Clay Conference, MacEwan (1962) covered much of the field of interlamellar complexes. Brindley and Hoffmann (1962) reviewed thoroughly the ideas on the orientation of organic molecules adsorbed on clay mineral surfaces. We also heard many specialized papers ranging from the small methylamine bentonite complexes of Rowland and Weiss (1963) to the molecular mountains of Pinck's (1962) proteins, enzymes and antibiotics on montmorillonite. With such thorough coverage, one might ask, what is left to be perspective about? The answer to that question is that, with the exception of the patent literature, less attention has been given in publications to

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the applications of organo-clay knowledge than has been given to the more fundamental aspects.

My purpose, then, in presenting this necessarily incomplete review is not merely to fly over some of the same territory so ably covered at the Ninth and Tenth Clay Conferences but also to contribute a bit of the industrial viewpoint to this fascinating subject of organo-clay chemistry.

In what follows, I shall try to reflect some of the reasons why I regard organo-clay chemistry somewhat as the great German chemist Wöhler, who synthesized the first organic compound, urea, felt about organic chemistry as recently as 1848:

“Organic chemistry . . . gives me the impression of a primeval tropical forest full of the most remarkable things. . . .” So, too, organo-clay chemistry promises a forest of “remarkable things”.

In considering the promise of organo-clay chemistry, we shall first examine very briefly some of the technical-historical aspects such as the hybrid nature of organo-clays and a suggested definition of organo-clays, and name a few of the outstanding scientists in organo-clay chemistry and indicate what contributions they made. Being from an oil company I have also included a listing of some areas of interest to the petroleum industry. Then, we shall examine some of the attractions of clay-organic systems—the factors that promise fruitful research. Next, I shall mention some of the concepts that serve to distinguish organo-clays from simple mixtures. An outline of some of the elements of clay architecture follows, and this is supplemented by an example of a surface coverage calculation, some evidence for the reactivity of clay at edge sites, the concept of clay-polymer bridges and some suggested types of clay-to-polymer linkages. We then note some of the twenty or more companies that have shown their interest in organo-clays by patenting their findings. Several areas of inadequate information are mentioned, a brief discussion is given of the influence of ionizing radiation on clays and organic materials and, lastly, areas where organo-clays may find new and profitable uses are indicated.

Chemistry

As we all know, the science of chemistry can be divided into two main branches: organic chemistry and inorganic chemistry. In the middle column of Fig. 1 are listed a few general indicators which differentiate these branches in an approximate way. Actually, there are exceptions to each characteristic, but they do suffice to give us our bearings in the great forest of presently known compounds. Thus, the organics are the carbon-containing compounds while all the other 101 elements are lumped in inorganic chemistry.

The organics go back to biological beginnings, the inorganics to minerals.

There are millions of known organic compounds and a relatively few thousand inorganics. In general, organic reactions go slowly in contrast to the usually fast inorganic reactions. The organics are relatively less heat stable than the inorganics; no organic can withstand heating to a red heat.

There are other distinguishing differences in respect to flexibility, elasticity,

solubility and hardness. The petroleum hydrocarbons and derivatives are characteristic organics and the clays are characteristic inorganics.

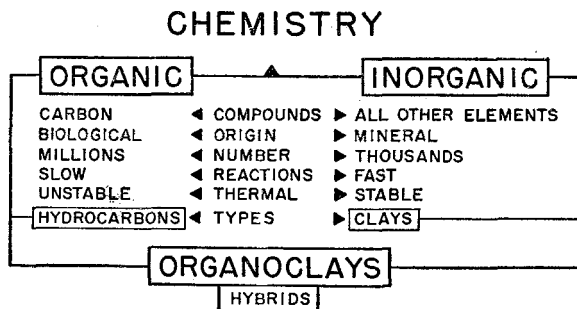
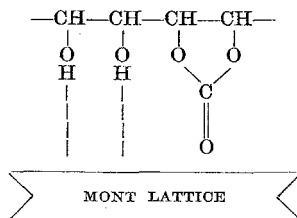


FIGURE 1.—Relationship of organo-clays to organic and inorganic chemistry.

As indicated in Fig. 1, the organo-clays are hybrid unions of organic and inorganic materials. The hybrids may be expected to have properties characteristic of both organic and inorganic compounds and, so, give rise to another large area of chemistry.

Definition of Organo-clay

Here we offer a broad definition of the term “organo-clay”, viz. “Organo-clays are reaction products of specific clay minerals with specific organic molecules involving the formation of chemical bonds.” That chemical bonds are involved may be inferred according to certain widely accepted criteria such as heats of reaction, stability toward distillation, and non-extractability of the organic function in normal solvents for the organic. These may be ionic bonds resulting from acid-base neutralization or simple ion exchange, or they may be strong adsorption-type van der Waals’ bonds, e.g. as in partially hydrolyzed poly(vinylene carbonate)-montmorillonite,



Very loosely associated aggregates of clay and organic materials are excluded, e.g. methane-montmorillonite at normal temperature and pressure.

Like most definitions, the above leaves much room for improvement. For the present, there can probably be no general agreement on the meaning of

such a broad term as "organo-clay", because even the term "chemical bond" is still being hotly debated (Mooser and Pearson, 1961; Cochran, 1961). For comparison, we may quote Glaeser's (1954) definition that "the term organo-clay is limited to the direct fixation of non-ionized molecules on clay by adsorption".

Some Leaders in the Field

Table 1 lists some of the principal contributors to organo-clay chemistry and sample areas of contribution. This is evidently not a complete listing since, for reasons of space only, the names of such first-rate scientists as

TABLE 1.—SOME PRINCIPAL CONTRIBUTORS TO ORGANO-CLAY CHEMISTRY

Name	Area of contribution
Barrer, R. M. (Barrer and Kelsey, 1961)	Thermodynamics
Bradley, W. F. <i>et al.</i> (1958)	X-ray studies
Brindley, G. W. (Hoffmann and Brindley, 1961)	Adsorption complexes
Cowan, C. T. (Cowan and White, 1958)	Ion exchange
Deuel, H. (1957)	Derivatives
Dodd, C. G. (Dodd and Ray, 1960)	Dye adsorption
Emerson, W. W. (1960)	Clay-polymer complexes
Giesecking, J. E. (1955)	Exchange adsorption
Greene-Kelly, R. (1956)	Sorbate architecture
Greenland, D. J. (Greenland and Russell, 1955)	Adsorption complexes
Grim, R. E. (1960)	Concepts and applications
Hauser, E. A. (Hauser and Kollman, 1960)	Patented applications
Hendricks, S. B. (1945)	Ion exchange concepts
Iler, R. K. (1955b)	Esters ("Estersils")
Jordan, J. W. (1960)	Derivatives ("Bentones")
MacEwan, D. M. C. (1948)	Structures of complexes
McAtee, J. L. Jr. (1959)	Ion exchange
Pauling, L. C. (1930)	X-ray structure of layer minerals
Ruehrwein, R. A. (1957a)	Polycation derivatives
Slabaugh, W. H. (Slabaugh and Kupka, 1958)	Cation exchange
Talibudeen, O. (1955)	Complexes with amino-acids and proteins
Uskov, I. A. (1960)	Filled polymers
Walker, G. F. (1958)	Interlayer complexes

I. Barshad, Dorothy Carroll, U. Hoffmann, R. Glaeser, E. W. Gluesenkamp, M. L. Jackson, W. D. Keller, C. E. Marshall, J. Méring, K. Norrish, H. van Olphen, A. Weiss and J. L. White are not included. Skimming the list we can certainly say that much of the bedrock of organo-clay chemistry was laid by Linus Pauling with his basic X-ray structure work and by Grim,

Bradley, Brindley and MacEwan among many others. Very important contributions in the strictly chemical area have been made by Giesecking, Hendricks and Hauser on the sorption of organic ions on bentonite, by Jordan with his classic study of the reaction of aliphatic amines with bentonite, and more recently by Iler of du Pont, Ruehrwein of Monsanto and Barrer in England in the area of industrial applications of organo-clays.

Oil Company Interests

As indicated above, oil companies have rather considerable interests in clays and especially in the phenomena occurring at clay-organic interfaces. Following are some of the areas of interest:

- (1) In lube oil refining to remove color bodies.
- (2) In catalyst activation and deactivation phenomena.
- (3) In drilling fluids as a basic component.
- (4) In reservoir mechanics as the principal chemically reactive rock influencing the flow of oil, water and gas; a most important factor in secondary recovery operations.
- (5) In well-maintenance as reservoir components whose chemistry must be considered in the planning of clean-out procedures.
- (6) In the interpretation of electric logs where account must be taken of the presence of clay in the mud cake. This is because the nature of the clay surface will determine the extent of its membrane electric potential contribution to the S.P. (self-potential) curve.
- (7) In exploration, the possible role of clay in the genesis of petroleum is of great interest.

Attractions of Organo-clays

Here are some of the chemical and economic attractions of the clay-organic complexes:

- (1) Because of the very large number of available reactive organic molecules the hybridization potential for chemical novelty is high.
- (2) The clay platelets in the 0.01–2 μ range can aptly be described as chemically reactive polymer-size rocks.
- (3) The possibility of synthesizing more thermally stable materials by clay-organic hybridization invites the effort.
- (4) There is no dearth of raw materials and no monopoly.
- (5) The penny-a-pound or less clay when used as the major component in an organo-clay permits using expensive organics.
- (6) And last, but not least, is that there is relatively little research activity—as yet—in this field; the chance of finding the new is high.

Reality of Organo-clays

By the “reality” of organo-clays, in accordance with my previous definition of organo-clay, I mean that the organic adduct is bonded *firmly* to the clay. This of course gets us back into the question of how strong is a bond that

binds? We can get a good feel for this bond strength by answering such questions as: is the organic part solvent-extractable, distillable or desorbable (under high vacuum)? Specific examples of such testing are found in the literature in the work of Jordan (1949) on the alkylammonium bentonites, in the tests by Barrer and Reay (1958) of Deuel's "phenyl" montmorillonite and in the impressive experiments of Emerson (1960) on the nature of the clay-polymer bonds formed by the interaction of calcium-montmorillonite with a wide range of polymers. Emerson found three types of association:

- (1) The first type of association is one in which the polymer is readily removable by N sodium chloride. This is interpreted to mean that the bond is formed by a precipitation complex with readily exchangeable calcium ions. Sodium alginate is such a polymer.
- (2) The second type of association is one in which the polymer is removable only by strong sequestering, e.g. with sodium pyrophosphate. The bond is made by forming a coordination compound with the less readily exchangeable calcium ion. Polyacrylamide is such a polymer.
- (3) In the third type of association the polymer is not removed by either N sodium chloride or sodium pyrophosphate. The bond is the hydrogen from polymer OH to plate SiO and is independent of valence of exchange ion. Polyvinyl alcohol is such a polymer.

And, finally, we consider the question of organo-clays as "fillers" or complex formers in polymeric systems. If the organo-clay forms a chemically crosslinked complex with the polymer matrix it will insolubilize or gel the system in a polymer solvent; if it behaves simply as an extender of the polymer, extraction in a solvent for the polymer will result in phase separation. Along these lines Uskov (1960) and co-workers at the University of Kiev are carrying on an interesting and continuing study of filled polymers. For example, they find that under their conditions, they can graft poly-(methylmethacrylate) on to a sodium montmorillonite backbone to the extent of 22 weight percent starting with the organic monomer, but that the grafting is not successful on the octadecylammonium derivative of this clay.

Architecture of Organo-clays

The papers of the symposium on clay-organic complexes (this Volume) have already provided us with an abundance of clay architectural detail. Here we note only briefly those elements of clay-organic architecture of interest to the application-oriented clay chemist. The primary factors of clay-organic structure are the shapes of the clay plates, their overall dimensions, whether they are reacted under conditions of unit platelet dispersion or in multiplatelet packets, how much surface area is available per ion exchange site, where the reactive sites are located (whether on the edges or on the basal surfaces), how the organic adduct is packed, whether aligned perpendicular or parallel to the plate, whether tilted or keyed into the hexagonal silicate oxygen holes or both, whether the concentration of organic adduct is such as to result in single,

double or multiple layering, whether the bonding is by ion exchange, covalent reaction, hydrogen bonding or van der Waals' adsorption and, in the case of very large organic molecules, whether or not copolymer-type bridges are involved.

As has been pointed out by Iler (1955a, p. 221), clay-organic reactions can lead to products of appreciable organic content. Take, for example, 100 g of montmorillonite with a surface area of 300 m²/g (3×10^4 m²/100 g) carrying a long-chain organic amine of molecular weight 300 and with a molecular

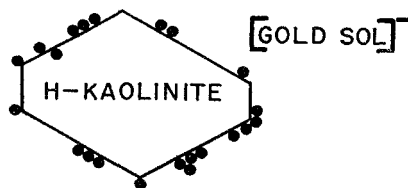


FIGURE 2.—Schematic representation of experimental evidence for the existence of positively charged edges in H-kaolinite; after Thiessen (1942) and Méring, Mathieu-Sicaud and Perrin-Bonnet (1953).

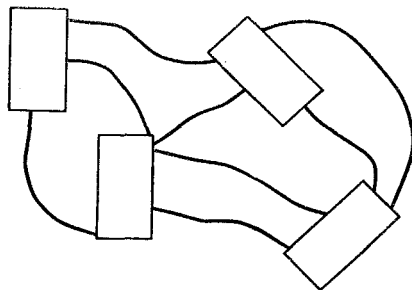


FIGURE 3.—Clay "copolymer"; after Michaels' diagram (1958).

cross-section of 30 Å²; the gram-molecular cross-section is 18×10^4 m² ($30 \times 6 \times 10^{23} \div 10^{20}$ Å²/m²). Coverage to a depth of only a monolayer requires 0.167 mole ($3 \times 10^4 \div 18 \times 10^4$) or 50 g of amine.

Figure 2 shows schematically one of the evidences for the existence of positively charged edges in hydrogen-kaolinite, namely, the observation in the electron microscope, originally by Thiessen (1942) and confirmed by Méring, Mathieu-Sicaud and Perrin-Bonnet (1953), that negatively charged gold sol particles congregate almost exclusively at the edges of the hexagonal plates.

Figure 3 shows Michaels' (1958) concept of long-chain polymers bridging between clay particles. This mechanism is used to explain the massive flocculation of kaolinite at polymer concentration levels as low as 0.001th of a weight percent based on clay.

Figure 4 depicts the three types of clay-to-polymer linkages discussed last year at this Conference by van der Watt and Bodman (1962) for the vinyl-acetate maleic anhydride aluminum montmorillonite complex.

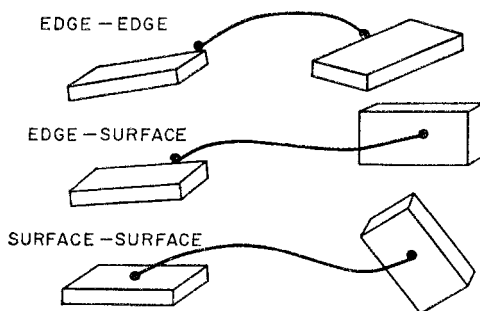


FIGURE 4.—Concept of clay-polymer links.

Company Interest in Organo-clays

A growing number of companies have shown their interest in organo-clays by patenting their findings and by their advertising literature. Here are but a few specific examples of companies and patent claims showing the wide range of applicability:

Allied Chemical (Cordier, 1957) claims formaldehyde-melamine resin-coated kaolin reinforces poly(diallylphthalate) molding compounds.

du Pont (Iler, 1955b) claims that *n*-butyl attapulgite improves the tensile and tear strength of natural rubber.

Eastman Kodak (Caldwell, 1960) claims that the ability of acrylonitrile fibers to hold dye is enhanced by including dodecyl-, octadecyl- or oleylamine bentonite in the spinning solution.

Elastic Colloid Research Corporation (Cohn, 1954) claims that olefin surfaced clays bearing allyl or oleyl groups are useful for cross-linking elastomers.

Esso Research and Engineering Company (Rehner, Wiese and Gessler, 1960) claims that cyclopentadienyl trichlorosilane clay reinforces butyl rubber.

General Tire (Te Grotenhuis, 1957) claims that olefinic clays can be made by reaction of clays with isocyanates bearing an unsaturated R group.

Gulf Oil (Brown, 1956; Brown and Giacobine, 1956) has a group of at least eight patents covering the use of the widest imaginable variety of organic cations as stabilizers for clay-containing regions adjacent to well bores and for stabilizing other clay-containing bodies. They also claim the use of these organic cations in fluids injected ahead of the main displacing fluid in a flooding method of oil recovery.

J. M. Huber (Van Volkenburgh, 1959) claims that urea-treated kaolinite makes polyvinylchloride resins and polyvinylidene chloride resins more color stable.

Libbey-Owens Ford-Glass (Cordier, 1953) claims that formaldehyde-melamine kaolinite reinforces unsaturated polyester molding compounds containing enoyl groups, that is, polymers with a carbon-carbon double bond followed by a carbonyl group.

Minerals and Chemicals-Philipp (Wilcox, 1961) has a patent that claims kaolin coated with polyamines as chemical products useful at high clay content in organic systems for maintaining the low viscosities desired in many processing operations.

Monsanto Chemical Company (Ruehrwein, 1957a) claims as chemical products the materials formed by adducting to montmorillonite the poly-cations containing organic basic nitrogen. An example of such a product is poly(vinyl pyridine) montmorillonite. Another interesting patent assigned to Monsanto by Ruehrwein (1957b) claims montmorillonite adducts of proton donating ethylenic polymers such as polyvinyl alcohol.

National Lead Company (Jordan, 1950, 1960) has the famous Bentone patents covering the use and preparation of long-chain fatty amine bentonites in paints and greases.

Shell Oil Company (Freeman and Peterson, 1961) has patented greases, including silicone base greases, filled with organo-metallic exchanged clays such as hectorite and montmorillonite. They are claimed to be stable toward ionizing radiation. The organo-metallics are ferrocenes, which are the metal ion derivatives of *bis*-cyclopentadienyl.

Union Oil Company of California (Nahin, 1953) has long been interested in improving oil base drilling fluids and has patents in this field.

Westinghouse Electric Company (Zukas, 1956) has found that hexadecyl- and octadecyl-bentonite stabilize the insoluble dicyandiamide catalyst used in the hardening of liquid epoxy resins.

Clearly many large industrial concerns appreciate the values that novelly modified clays may have for them in the form of new products and processes. The patented refinements have enlarged the field to the point that the U.S. Patent Office now has classifications distinguishing between clays as fillers and modified clays as compounds.

Needed Research

Here we indicate in the broadest terms some of the large areas of inadequate information in the organo-clay field. There are some really good opportunities for basic research with good chance of the results leading to practical application. Thus, in the area of new derivatives we need information on more diverse and characterized derivatives. We should study the reaction capabilities of homofunctional and multifunctional derivatives as a function of the degree of substitution of one functionality by another; comparison of organo-clays synthesized in very dilute so-called "ideal" suspensions with those made in more concentrated suspensions would be interesting; mixed lattice derivatives are needed; the study of homologous series, with the possible exception of the amines, has hardly been touched.

Study of the nature of the organo-clay bonds is still a very attractive area.

Studies of mechanical and chemical decompositions, proof-of-structure studies along the lines of Barrer's "phenyl" montmorillonite and Emerson's clay-to-polymer bonds, methods of synthesis comparing ion-exchanged preparations with acid-base neutralizations would be useful contributions. The analytical chemistry of clay-organic complexes presents the chemist with an almost infinite variety of challenging problems. Thus, the effect of the clay surface on infrared spectra of organic structures has already been studied in some detail, but the field is still very young and in need of many more answers than we now have. Tests of older methods and development of new methods are needed for determining organic functions on clays—double and triple bonds, carboxyls, carbonyls, and all the others; effects of concentration of complexed organic functionalities in relation to particular methods of analysis are not known; more study of the methods of determining hydrogen ion exchange capacity is needed.

One of the most interesting areas of inadequate information is the area of edge-surface chemistry, that is, that part of clay chemistry which concerns itself with the relative degree of reactivity of the edge and surface sites in respect to a given substrate. As has previously been shown in organic polymer chemistry this calls for the investigation of reactivity ratios. The basis for this concept of different reactivities of interlayer and edge sites has been laid in the recent papers of Garrels and Christ (1956), Blackmon (1958), and Pommer and Carroll (1960) in their studies of the pH titration curves of hydrogen clays. It was suggested that cations are more strongly held at the edges than on interlayer surfaces. Similar studies of the neutralization of clay-polymeric electrolytes would be useful.

In copolymerization we have another area of inadequate knowledge of tremendous depth. The general idea of putting polymerizable organic groups on clays and then polymerizing the resultant derivatives with themselves or with other organics is discussed in the patent literature by Hauser and Dannenberg (1946), Te Grotenhuis (1958) and others. This field is unquestionably a fertile one for continuing research. For example, just last year Bisque (1962) at this Conference described the polymerization of clay by silicification with dimethylsilane vapor.

The irradiation of clays and clay-organic systems is another area in which research information is meager. Metz (1958) at Brookhaven has stated that incorporation of mineral fillers enhances the radiation stability of the base plastic. Caffrey and Allen (1958) and Allen and Caffrey (1960), also at Brookhaven, found that the radiolysis of normal pentane was profoundly altered in the presence of montmorillonite. For example, thin-film radiolysis on montmorillonite gave an approximately 80-fold increase in isobutane over that obtained by irradiation of bulk *n*-pentane at the same dose.

So you can see that the products of irradiation of clay-organic sorbed systems look very interesting. There is space only to mention the studies of radiation-induced ion molecule reactions on clays, the investigation of structure changes in irradiated filled plastics and the use of irradiated organo-clays as polymerization initiators.

Figure 5 indicates some possible effects of ionizing radiation on clays and organic materials. On the left we have an aggregate or "booklet" of kaolin the individual platelets of which are thought to be held together by hydrogen bonding between the silanol groups of one plate and the aluminum oxide oxygens of the adjacent plate. The 1 Feb. 1960 issue of *Chemical and Engineering News* reported that C. Orr and W. J. Corbett at Georgia Institute of Technology found that radiation will break down these kaolin stacks. I have presumed this means the stacks are "de-booked" into units with few platelets or even into single plates.

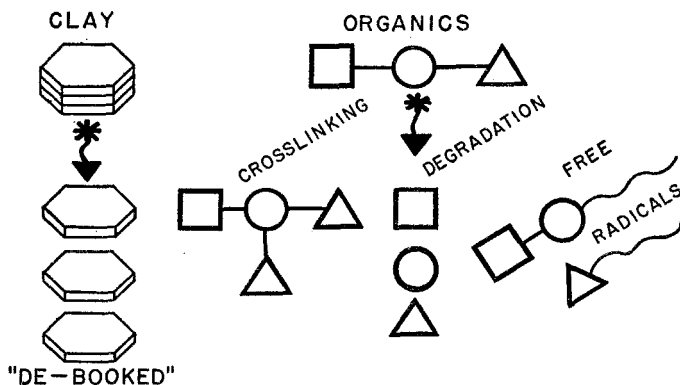


FIGURE 5.—Schematic representation of some possible effects of ionizing radiation on clays and organic materials.

The right-hand side of this figure is a schematic of some effects of radiation on organics. The reactions of cross-linking, degradation and scission into free radicals are such typical effects and these furnish the fuel for an infinity of new compositions and arrangements of clay-organic complexes.

Applications

Here we list some areas of application of clay-organic compositions. Levine (1962) of the Telecomputing Corporation has pointed out the route of improving polymer-to-metal bonds by reacting heat-stable organic polymers with reactive inorganic reagents. Clay-organic complexes in soil conditioning have been studied extensively through the work of de Mello, Hauser and Lambe (1953), Lamb and Michaels (1954), Hedrick and Mowry (1952) of Monsanto, and others. Their uses as insulation and sealants in building are possibilities. Mention is made of such uses as stationary phases in gas chromatography (Cowan and Heartwell, 1961), gellants in paints, strippable films (British Thomson, 1941), colorants, structural hydraulic fluids in shock absorbers (Agnello, Morris and Gunn, 1960), anti-rad agents in plastics, ablatants in nose-cones, viscosity control in polyester resins (Georgia Kaolin, 1961), reinforcing fillers in elastomers, oil base drilling fluid modifiers, dye receptors in fibers, catalyst templates (Pauling, 1949), carbonless typing paper (National

Cash Register, 1957), beater additive in paper making (Gluesenkamp, 1957), and many others.

In Perspective

“By its very nature a really new idea is hardly ever practical. Only its development will make it practical.”

This is basically how I regard some of the clay-organic concepts mentioned here today. Most of them need a *vast* amount of development to become practical. To be reasonably successful in predicting the future of applied clay-organic science I believe we should not lean too heavily on our present knowledge of clays. We must be willing to venture extrapolations from other areas of materials research and apply them with good technical sense to this area of macrosilicate science. Such attempts to predict the directions of clay research should in themselves be considered as important contributions to clay science. Perhaps a paper “Clay Science in the 21st Century” would help generate leap-frogging advances in this field. In this talk we have noted some potentially practical ideas, and some of them will be developed into important components of tomorrow’s technology. The ingenuity of our scientists and science-oriented managements guarantees it.

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