[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Color Reactions between Clays and Amines[1]

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A study of the discolorization of white sidewall tires has led to the discovery of *brilliant* color reactions between a number of organic compounds used as antioxidants in the rubber industry and different clay minerals.[2] This paper concerns itself with a more detailed study of this phenomenon.

Since it was found that all the rubber antioxidants which gave color reactions with the clays were amines, it was first desirable to ascertain whether the reaction is dependent on the presence of nitrogen as such, or whether an amino group is essential. Furthermore, it seemed of importance to determine whether the reaction occurs with aliphatic as well as aromatic amines. Finally, it was considered of value to establish as many methods of bringing the reaction about as possible.

The original experiments using clay and rubber antioxidant were limited to the formation of the color by allowing the dry clay and dry antioxidant to react with each other. The reaction, caused by direct contact or due to the vapor pressure of the antioxidant at room temperature, was slow and in the latter case confined to the exposed surface of the clay.

Since then it has been ascertained that the color—all shades of the spectrum have been produced—can be developed by either grinding the dry components together in a mortar or by mixing the clay with the reactant in the presence of a few drops of water. If the reactants are liquids, the color will appear immediately upon contact with the clay. In the case where water-soluble salts of the reactants are available, the color will appear immediately if the clay is added to the aqueous solution. Special care was taken to purify all chemical reagents as highly as possible.

We have listed in Table I a great number of compounds together with the color they form in combination with Wyoming bentonite (Al–Si–montmorillonite) both in basic and acid condition. All basic reactions were performed by either mixing the liquid amines with the clay or by adding a few drops of water to the dry mixture or by mixing the dry amine into clay hydrogel. In the acidic range a hydrogel of an acidified clay was used, to which either the liquid or solid amine was added.

TABLE I

No.	Compound	Basic color	Acidic color
1	Acetanilide	...	...
2	Acetophenone, *p*-amino-	Green	Yellow
3	Ammonia	...	...
4	Aniline	Green	...
5	Aniline, *p*-aminodimethyl-	Blue	Pink
6	Aniline, *p*-aminodiethyl-	Tan	Green-blue
7	Aniline, *p*-bromodimethyl-	Green	...
8	Aniline, diethyl-	Green	...
9	Aniline, dimethyl-	Green	...
10	Aniline, ethyl-	Green	...
11	Aniline, methyl-	Green	...
12	Aniline, *m*-nitro-	...	...
13	Aniline, *p*-nitro-	Green	...
14	Aniline, 4-nitro-2-chloro-	Green	...
15	Aniline, *o*-nitrodimethyl-	Orange	...
16	Aniline, *p*-nitrodimethyl-	Yellow	...
17	Aniline, *m*-nitromethyl-	Yellow	...
18	Aniline, *p*-nitromethyl-	Yellow	...
19	Aniline, *p*-nitrosodimethyl-	Brown	Yellow
20	Aniline, tribromo-	...	...
21	Anisidine, -*o*-	Pink	Blue
22	Anisidine, -*p*-	Purple	Blue
23	Anthranilic acid	...	Pink
24	Anthraquinone, 1-amino-(red)	No change	
25	Anthraquinone, 2-amino-(red)	No change	
26	Benzene, *p*-aminoazo-	Brown	Pink
27	Benzidine	Blue	Yellow
28	Benzoic acid, acetyl-*o*-amino-	...	...
29	Benzoic acid, *p*-amino-	...	Yellow
30	Benzylamine	...	...
31	Cyclohexylamine	...	...
32	Dianisidine-*o*	Green	Pink
33	Diphenyl, *o*-amino-	...	...
34	Diphenyl, *p*-amino-	Weak green	...
35	Diphenylamine	Blue	Blue
36	Diphenylamine, acetyl-	...	...
37	Diphenylamine, 4-amino-	Yellow	Blue
38	Diphenylamine, isopropoxy-	Green	...
39	Diphenylmethane, *p*-diamino-	Pink	...
40	Diphenylmethane, tetramethyl-*p*-diamino-	Gray	...
41	Hydroquinone	...	...
42	Metanilic acid	...	Pink
43	Michler ketone (tetramethyldiaminobenzophenone)	Green	Yellow

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(1) Presented before the Colloid Division, American Chemical Society, at Cincinnati, Ohio, April 9, 1940. This paper is largely a condensed review of the Master of Science thesis of M. B. Leggett.

(2) A brief report of the earlier observations, made jointly with T. J. Cater, Jr., was presented by one of us (E. A. H.) before the Division of Colloid Chemistry at the meeting of the American Chemical Society held in Boston on September 11–16, 1939.

TABLE I (*Concluded*)

No.	Compound	Basic color	Acidic color
44	Monoethanolamine	...	...
45	Naphthylamine, α-	Green	...
46	Naphthylamine, β-	Pink	...
47	Naphthylamine, di-β-	...	...
48	Naphthyl, di-β-*p*-phenylene-diamine	Pink	...
49	Naphthylamine-1 Trisulfonic acid-3,6,8	...	...
50	Nitrobenzene	...	...
51	Phenetidine, *o*-	Pink	Blue
52	Phenetidine, *p*-	Purple	Blue
53	Phenetidine, *p*-acetyl-	...	...
54	Phenol, acetyl-*m*-amino-	...	...
55	Phenol, acetyl-*o*-amino-	...	...
56	Phenol, acetyl-*p*-amino-	...	...
57	Phenol, *p*-amino-	...	...
58	Phenylethylmethanolamine	Green	...
59	Phenylmethanolamine	Green	...
60	Phenyl-β-naphthylamine	Pinkish green	...
61	Phenylene-*m*-diamine	Green	...
62	Phenylene-*o*-diamine	Yellow	Pink
63	Phenylene-*p*-diamine	Purple	Pink
64	Pyridine	...	...
65	Quinone	...	...
66	Resin "D"	...	...
67	Sulfanilic acid	...	...
68	Tolidine, *o*-	Blue-green	Yellow
69	*p*-Toluenesulfonylmethyl-aniline	...	...
70	Toluidine, *m*-	Yellow	Orange
71	Toluidine, *o*-	Yellow	Orange
72	Toluidine, *p*-	Pink	...
73	Toluidine, *m*-acetyl-	...	...
74	Toluidine, *o*-acetyl-	...	...
75	Toluidine, *p*-acetyl-	...	...
76	Triethylamine	...	...
77	Triphenylamine	...	...

A detailed survey of Table I reveals the following facts: Only certain amines of the aniline type give the color reaction (1). Similar aromatic compounds with the nitrogen attached to the benzene nucleus give various colors depending on the type of substituents present (70, 71, 72; 21, 22; 51, 52; 61, 62, 63; 27,[3] 32, 68). Aliphatic amines (3, 44, 76) as well as saturated cyclic amines (31) give no reaction. Nitrobenzene (50) and heterocyclic nitrogen compounds (64, 66) and compounds with the amino groups removed from the benzene ring (30) are non-reactive. An acetyl group on the nitrogen inhibits color formation (1, 28, 36, 53, 54, 55, 56, 73, 74, 75). Alkyl groups substituted in the amino group intensify the color (8, 9, 10, 11). Aryl groups exhibit a similar effect (35, 37, 38, 60). NH_2 as a ring substituent intensifies the color (61, 62, 63; 5, 6, 8, 9). NO_2, SO_3H, COOH, R, OR, acetyl, Br, OH reduce or inhibit color formation (7, 12, 13, 16, 17, 18, 20, 23, 29, 33, 34, 39, 40, 42, 45, 46, 49, 57, 67, 70, 71, 72). The position of methoxy and ethoxy groups is important. In ortho position (21, 51) they lighten the color; in para position (22, 52) they deepen it. Compounds of the benzidine type (27, 32, 68) and the naphthylamines (45, 46, 47, 48, 49, 60) give deep colors. The color will be the lighter the more acidic the ring substituent.

The color is specific to the amine and can be produced with all reactive types of clay (bentonite, fuller's earth, kaolin, zeogel, etc.).

The benzidines give blue, anilines green, and toluidines, pink or yellow colors.

The intensity of the color depends on the type of clay. Zeogel, bentonite, fuller's earth, kaolin, etc., form colors of decreasing intensity in the order given. China clays and illites react only slightly. Powdered silica, silica aerogel, aluminum oxide, ground mica and ignited bentonite are non-reactive.

The fact that so colored Wyoming bentonite will still swell in water and permit base-exchange suggests that the color reaction is not to be regarded as a simple base exchange phenomenon. The addition of excess amines results in making the color dull or even black. By either adding more clay or simply washing the excess amine off, the brilliancy of the color reappears immediately. To test the possibility that the color might be due to a reaction between the amine and oxygen or an oxidizing agent adsorbed or entrapped in the clay structure, the experiments were repeated with carefully prepared oxygen-free pure clay. No change in the character or intensity of the colors could be observed.

It is interesting to note that where the color was obtained by mixing clay and solid amine in the presence of water the products return to their original colorless state on drying. However, the color can be restored on wetting.

In certain cases the change in color on drying is a process involving progressive lightening of color. *o*-Tolidine dries from blue to green to yellow to colorless, as do benzidine and *o*-dianisidine. The compounds containing only one aromatic ring dry out directly to the colorless state. The color changes from the wet to dry state are the same as those obtained by adding acid to the colored clay.

[3] G. Stern of the U. S. Bureau of Mines informed us during the course of this work that he had observed a strong color reaction between benzidine and bentonite in the presence of water.

The liquid amines apparently hold their color even when dry and the colors produced by grinding dry clay and solid amine also persist without added moisture. In the cases where the clay is added to the amine hydrochloride, the acid apparently base exchanges with the clay. The amine, no longer solubilized, then contacts the clay surface. There is no evidence that the color can exist independently of the clay. Whenever a suspension of the colored clay is made in any liquid the color settles with the clay, leaving a clear supernatant liquid.

It has not been possible to remove any of these colors from the clay and maintain them in solution or in the solid state. Attempted extraction[4] of the green color of dimethylaniline with acetone gave a colorless wash liquid which proved to be acetone and unreacted amine. The clay was colorless and found to be unaltered in its properties. Similarly, benzidine and clay were recovered from their blue reaction product.

Dimethylaniline is a notable example of the color reactions in that it gives first a green color and then, either after standing or on heating, a blue color and finally, a purple color.[5] The last shade is different in character from those previously mentioned, it being no longer reversible and definitely associated with the clay. It exists as well in the dry state as in the moist and is unaffected by mild heating. It cannot be removed by solvent extraction, but if it is treated with acid the purple clay turns to a dark green in color; when washed with acetone or dioxane, the wash liquor is purple although the clay remains green. Water washing of either the purple or green clay produces no detectable change in the clay or in the wash liquor. This purple clay has lost its ability to swell in water and no longer forms colloidal suspensions in water.

If environmental conditions are changed, the reaction is thereby noticeably affected, revealing the following noteworthy trends.

Mineral and organic acids either inhibit or lighten the color. For example, *o*-tolidine (68) shifts from blue to yellow, aniline from green to colorless (4), *p*-aminodimethylaniline (5) from blue to pink. Bases added to the colored clay in neutral media have no effect, but when added to the acidified clays restore the original basic color. Thus, benzidine (27) can be shifted from blue to yellow and back to blue any number of times by additions of acid and base, respectively. Reducing agents, such as stannous chloride and formaldehyde, reduce the color or destroy it completely, just as do the acids. If one adds an oxidizing agent to such a mixture the color is restored. Potassium chlorate will restore the pink color to acidic *p*-aminodimethylaniline (5) which has been reduced to the colorless state with stannous chloride. If one adds either the acid or reducing agent to the clay before the amine is introduced, the lighter or colorless state is immediately obtained and can be shifted to the darker shade by suitable addition of a base or an oxidizer. The presence of solvents for the amines reduces the amount of color; the deficiency is proportional to the solubility of the amine in the solvent and to the amount of solvent present.

It is today generally assumed that the appearance of color in a compound results from a special type of resonance and the depth of the shade is considered a measure for this phenomenon. With the type of compounds which have been shown to give the brilliant clay colors, one can easily visualize the provocation of resonance.

In the case of the amines and the clay, it has been shown that no reaction *products* are attainable for analysis, but that the original reactants return on separation. Therefore, one cannot ascribe the color to any *addition* to the nitrogen atom. However, that this atom is responsible for the reaction is indicated by the activity of compounds with ring substituents in all possible positions, particularly by the para substituted dialkyl anilines. Moreover, the action of excess acid in inhibiting color formation and the return of the color in basic solution suggests that the nitrogen in the lower state of valency is the active factor.

The most probable cause for color formation in compounds of this type would be oxidation. Atmospheric oxygen colors most of the compounds used. However, it does not give the shades found on clay. The color formation with clay is favored by alkaline media and inhibited or lessened by acids. Moreover, the presence of acidic substituents in the molecule lessens the tendency to form color, while basic substituents promote deeper

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(4) All extractions were done in the cold to prevent formation of the usual amine oxidation products.

(5) After presentation of this paper, there appeared in *Chemical Abstracts*, **34**, (April 10, 1940) a review of a paper by A. Eisenack, in *Zentr. Mineral. Geol.*, **1938A**, No .10, 305–308, outlining preliminary observations on reactions similar to this one. The author found essentially the same phenomenon as this further reaction of dimethylaniline using several aromatic amines.

shades. Reducing agents inhibit the reaction. Oxidizing agents favor it. All these facts suggest that oxidation is the actual cause for the appearance of color.

The possibility that adsorbed or occluded oxygen or an oxidizing agent is responsible for the reaction already has been eliminated. However, the surface of a clay particle has many points of unsaturation where metallic atoms have unsatisfied residual valences, created when the clay crystal is ruptured. These metallic atoms are part of the lattice structure of the clay and therefore cannot be removed.

The metallic atoms involved will be those which occur in the unsubstituted crystalline structure, as the substituted metals of lower valence are already saturated and create the excess negative charges as the clay particle to which base-exchange is attributed.

The reaction might be explained as follows. The amine after it is brought into close contact with the clay particle is adsorbed by the available unsaturated metal groups on the surface. One of the unshared electrons in the nitrogen outer shell is transferred into the crystal structure, setting up an unbalanced force field in the amine. This condition provokes resonance in the amine and the quinoidal structure is obtained. In this way the amine acts in a similar manner to what would be the expected action of a reducing agent and it is easily seen why reducing agents inhibit the reaction, *i. e.*, the reducers having more readily transferred electrons act as donors rather than the amine. Similarly, this reaction could occur with aliphatic and heterocyclic amines, without formation of colored compounds, and the aromatic amines added after these others would not react.

As long as the aromatic nitrogen atom and the unsaturated metallic atom are in close contact, color will persist. On separation the nitrogen becomes stabilized and the clay is restored to its original state. Nitrogen with all electrons shared, such as in nitrobenzene and the amine salts (if their salt acid is not removed) will not be capable of undergoing this reaction.

It is probable that some association between resonating molecules will occur in the close-packed adsorbed layer on the surface of the clay. This would tend to give deeper colors and account for the greens in the benzene derivatives where ordinarily imine molecules would be yellow. This association would not be permanent and one would expect to be able to regain unreacted amines, as actually is the case. If the compound were highly reactive, however, one might expect a coupling by some means between the molecules and this would explain the formation of the purple clay from the green dimethylaniline product.

In the case of the compounds which exhibit different colors in acidic and basic media, the extent of the resonance will be the controlling factor in color. Benzidine in basic media gives a deep blue color, in acid a yellow color and in highly acid solutions no color at all. Preliminary tests seem to indicate that the color is determined by the amount of acid salt formed with the amino groups. Thus, in basic media no salt formation occurs and the resonance goes through the two rings of the biphenyl nucleus, resulting in a deep blue. If sufficient acid is added to form salt with one-half the amine present, the resonance is restricted to one ring and, since association is prevented spatially, the yellow color typical of imine compounds is produced. More acid forms salt with all of the amino groups, no resonance is induced, and a colorless state results.

The experimental data and the hypothesis as offered point toward various possibilities to stabilize the colors obtained. Work in this direction is being continued as well as a more detailed study of the actual mechanism of the color reaction. It is hoped that these results can be presented in the very near future.

Summary

The formation of colored compounds on clay has been shown to be the result of a reaction between clay and aromatic amines.

The influence of various substituents, acid and bases, is discussed.

A preliminary hypothesis explaining the mechanism of the reaction is advanced and further work outlined.

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