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MEMORANDUM REPORT #M-637

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THE USE OF ORGANO-TITANIUM AND ORGANO-ZIRCONIUM COMPOUNDS IN FINISHES

INTRODUCTION:

The intention of the Pigments Department to release organic titanates to the chemical industry (1) coupled with the information released by National Lead Company concerning the use of these materials in finishes (2, 3) makes it imperative that we review critically F & F's position in this field. For some time F & F has made attempts to utilize organic titanates (4-11) but has never obtained results which encouraged a major effort.

SUMMARY AND CONCLUSIONS:

Examination of available information concerning the use of organic titanates in finishes indicates that the following desirable results or properties are obtained:

(1) Fast, room temperature cure
(2) Increased hardness
(3) Increased acid, alkali, solvent and moisture resistance
(4) Anti-wrinkling properties
(5) Increased dielectric strength
(6) Improved adhesion (questionable)

Of the desirable results produced by organic titanates, the

most important is fast room temperature cure. The degree of improvement in hardness and chemical resistance does not appear to be unusual; it is no greater than one would expect if some other crosslinking agent were employed e.g. a diisocyanate.

The following undesirable features have been noted when titanates are used in finishes:

(1) Initial yellow color of films containing titanates

(2) Photodegradative effect of titanates on organic polymers

(3) Poor can stability of compositions containing titanates

(4) Poor flexibility of films containing titanates

The yellowing and photodegradative effect of titanates are serious drawbacks to their use in finishes. The Pigments Department feels that these two problems can be solved. They point out that they have encountered them before and have always obtained acceptable solutions. In view of the seriousness of these drawbacks the initial objective of our research in this field should be to remedy these defects. They might be overcome by using additives such as alkyl antimonites or replacing the titanates by alkyl zirconates.

A further objective should be to explore the heretofore unexamined stable chelates of titanium and zirconium as novel elevated temperature curing agents. This program, outlined at the end of the memorandum, could be included in the existing project P-3567, Organic-Inorganic Polymers.

It is believed that the problem of can stability can be solved by proper choice of solvents and that film flexibility can be improved by selecting the right polymers. Work on these aspects of the problem would be warranted only if initial yellowing and photodegradation is overcome.

DISCUSSION:

The desirable properties imparted to polymers by incorporation of organic titanates as reported by the National Lead Company and the Pigments Department are:

(1) Fast, room temperature cure

(2) Increased hardness

(3) Increased acid, alkali, solvent and moisture resistance

(4) Anti-wrinkling properties

(5) Improved application properties

(6) Increased dielectric strength

(7) Improved adhesion

Curing of polymers by alkyl titanates is believed to proceed according to the following schemes:

(a)

$$2\ \text{Polymer-OH} + \text{Ti(OR)}_4 \rightleftharpoons \begin{matrix}\text{Polymer-O}\\ \text{RO-Ti-OR}\\ \text{Polymer-O}\end{matrix} + 2\text{ROH}$$

(b)

$$2\ \text{Polymer-COOH} + \text{Ti(OR)}_4 \rightleftharpoons \begin{matrix}\text{Polymer-COO}\\ \text{ROTi-OR}\\ \text{Polymer-COO}\end{matrix} + 2\text{ROH}$$

(c)

$$2\ \text{Polymer-OOCR'} + \text{Ti(OR)}_4 \rightleftharpoons \begin{matrix}\text{Polymer-O}\\ \text{RO-Ti-OR}\\ \text{Polymer-O}\end{matrix} + 2\text{R'COOR}$$

Alkyds containing alkyl titanates may cure by either reactions (a) or (b) or a combination of both. Polyvinyl acetate cures by reaction (c). All reactions are equilibrium reactions and proceed to completion producing crosslinks when alcohol or ester is removed. Obviously the two remaining alkoxyl groups can react with more polymer resulting in further crosslinking. The most desirable feature of curing by alkyl titanates is

that the reaction proceeds at room temperature providing the alcohol or ester formed is volatile. Since butyl alcohol and isopropyl alcohol are quite volatile, rapid room temperature cures of alkyds are obtained with either tetrabutyl or tetraisopropyl titanate. Another desirable feature is that the crosslinking reaction can be repressed by addition of alcohol which makes it theoretically possible to obtain can-stable finishes.

Titanates may be used to cure polymers at elevated temperatures as well as at room temperature. In (a), (b), and (c) above use of elevated temperatures will probably yield more tightly crosslinked films as a result of reactions involving the third and fourth alkoxy radicals. In the case of the chelates of alkyl titanates having a high degree of stability it is quite possible that curing may occur only at elevated temperatures. Use of titanium chelates as curing agents is novel and relatively unexplored. Therefore, they should be investigated regardless of our ability to overcome the problem of yellowing and photodegradation, since they may be useful in fields where these forms of failure are not important. Two engaging ideas along this line are: (1) the use of the stable water-soluble chelate obtained from the reaction of two moles of lactic acid with one mole of tetrabutyl titanate to crosslink water-soluble polymers containing either hydroxyl or carboxyl groups; (2) the use of the stable chelate obtained from the reaction of two moles of 2-aminoethyl ethanolamine with one mole of tetrabutyl titanate to crosslink Epons (2, 3).

The National Lead Company reports that a soya alkyd containing 10% tetrabutyl titanate dried faster to a film which was harder and more resistant to xylene, moisture and alkali than the unmodified soya alkyd film. Similar results were obtained with a phenolic, ethyl cellulose and an Epon. The improvement in properties might be attributed to the higher degree of crosslinking. In the case of the soya alkyd, titanate crosslinking is superimposed on the crosslinking through unsaturation and the net result as expected is a faster cure to a more inert film.

Anti-wrinkling properties of titanates have been well demonstrated by Huntsberger and Kluberton (4, 5).

Better application properties (freedom from silking, sagging, etc.) probably result from fast film set-up through titanate crosslinking.

Improved dielectric strength results in the case of all polymers that the National Lead Company crosslinked with tetrabutyl titanate. The polymers include a phenolic, a vinyl, ethyl cellulose and an Epon. This would be important where a polymer was being considered for an electrical application.

The Pigments Department claims improved adhesion from the use of titanates in polymers. This claim has not been substantiated in the majority of systems examined by F & F and where improved adhesion was observed the results were erratic (5).

Less well defined reasons for attempting a research program on organic titanates are that they are readily available and Company products. Furthermore, it should be a simple matter to apply the know-how acquired under a titanate research program to the analogous zirconates. Alkyl zirconates probably possess many of the attributes of titanates without the objectional yellowing and the catalytic effect on photodegradation. Zirconium is not a particularly rare element and the compounds are becoming increasingly available, since the metal is used as a construction material for atomic reactors. It can be anticipated that the present high cost of alkyl zirconates will decrease.

The following undesirable properties have resulted from the use of alkyl titanates in finishes compositions:

(1) Initial yellow color

(2) Poor durability (due to photodegradative effect of titanates)

(3) Poor can stability

(4) Poor flexibility

Conversations with Dr. Seidel and Dr. Haslam of the Pigments Department and the information released by the National Lead Company (2, 3) indicates that all of these objections may be

overcome.

Initial yellow color and poor durability are probably interrelated. Titanium is known to form an intense orange-yellow peroxytitanate which may contribute to the initial yellowness of films containing organic titanates. In addition, titanium linked through oxygen with a vinyl group is known to be colored, e.g. phenoxytitanates are intense red. Apparently not all films have this objectional yellow color since the National Lead Company states that a film of ethyl cellulose and tetrabutyl titanate, 1:1, is water-white. The peroxytitanate is even more objectionable in our opinion because it converts to a redox system

$$(Ti^{+III} \rightleftharpoons Ti^{+IV})$$

which may participate in the degradation of the film during exposure. Dr. Seidel and Dr. Haslam point out that the Pigments Department have previously faced these problems and have always obtained satisfactory solutions. They stated that yellowing and photodegradation were eliminated in a mixture of cotton and tetrabutyl titanate by incorporation of an antimony ester and suggested that perhaps the ester would have the same effect in the case of finishes. It is obvious that this is a serious problem and must be solved before organic titanates can be considered for unrestricted use in finishes.

Poor can stability has resulted largely from a lack of understanding of the reactions and interactions which can occur when polymer is mixed with organic titanates. The National Lead Company and the Pigments Department have evidence which indicates that can stable systems can be obtained.

Mixtures of organic titanates and polymers yield films which have limited flexibility. When the titanate to polymer ratio is high very brittle films are obtained. This difficulty can be overcome by using only polymers that have a high degree of flexibility and by using low concentrations of organic titanates in preparing finishes.

In view of the seriousness of the yellowing and the photodegradative effect of titanates and the uncertainty concerning means of supressing these effects, it is recommended that these aspects of the problem be worked on first, together

with a limited amount of scouting on the chelates. This work, which should be undertaken immediately, is indicated under Program and could best be accomplished by including it as an objective under Project P-3567, Organic-Inorganic Polymers.

PROGRAM:

1. Determine whether yellowing and photodegradation of films containing titanates can be eliminated. (a) By methods suggested by the Pigments Department e.g. use of alkyl antimonites in conjunction with titanates. (b) By use of zirconates rather than titanates.

2. Examine the unexplored stable titanium and zirconium chelates as novel elevated temperature curing agents.

3. Give the best compositions a thorough evaluation including outdoor exposure.

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