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MARSHALL LABORATORY
October 23, 1952

MEMORANDUM REPORT NO. M-513

PIGMENTS DEPARTMENT - TITANIUM ORGANICS

Introduction:

The Pigments Department has worked on titanium-organo compounds over the past ten years, and during this period, they have offered numerous samples to the F. & F. Department for evaluation. These titanium organic compounds have comprised three types: (1) the titanium esters, $Ti(OR)_4$, (2) the titanium acylates

$$R'O\left[-\underset{OR'}{\overset{O_2CR}{TiO}}-\right]_x R' \quad \text{or} \quad HO\left[-\underset{OH}{\overset{O_2CR}{TiO}}-\right]_x H$$

and (3) the titanium chelated esters, such as octylene glycol titanate and titanium glycolate.

Most of our experimental work has been done with the titanium esters, particularly the lower esters, tetraisopropyl titanate (TPT) and tetra n-butyl titanate (TBT). Considerable experimental work has been done on the titanium acylates, such as titanium soy acylate, titanium linseed acylate and titanium stearate. Some work has also been done with the chelated esters.

This experimental work has been done by many people in different groups in connection with specific problems. The purpose of this report is to summarize this work to date.

Summary:

The titanium-organo compounds have been tested for various purposes, the more important of which were:

1. As agents to improve adhesion.

2. As agents to produce insolubilization or fast set.

3. As agents to reduce blistering of house paint.

4. As constituents of house paints to improve durability characteristics.

5. As modifiers of alkyd resins.

6. As constituents of "Duco" furniture sealers.

7. As agents to reduce wrinkling.

8. As pigment dispersing agents.

9. As crosslinking agents for U-F and polyvinyl acetate plywood adhesives.

10. Miscellaneous applications.

With the exceptions noted below, the results of this work have been negative. Newburgh and Flint Laboratories have also worked with the titanium organics, but so far have not found any practical uses for them.

Following Pigments Department's recommendations, a considerable amount of unsuccessful work was done with a 1-2% solution of tetraisopropyl titanate in anhydrous isopropanol as an agent to improve adhesion. The Pigments Department now states that tetraisopropyl titanate, used in this way, is not effective for this purpose unless the relative humidity at the time of application is below 40%. Very recently, however, R. J. Sheppard has found that a solution of 4.5% TPT and .5% OA in toluene, applied as a wash coat over 64-1690 Sheet Metal Primer or over 683-1196 Body Surfacer, definitely improves the adhesion of the OA topcoat to these two undercoats. The improved adhesion has been spotty and further work is being done to establish the effect of humidity and other factors on the reproducibility of the results.

Tetra n-butyl titanate is an effective fast setting agent when applied over a castor oil alkyd film, but the rapid hardening is a surface effect only and through hardening is slow at room temperature. However, this effect might be utilized in producing a fast setting printing ink, where film thicknesses are of the order of .1 mil.

Isopropoxy titanium stearate is the most effective agent so far found for reducing moisture migration in wood. Isopropoxy titanium oleate used as a primer on new wood reduces the blistering of #40 Outside White significantly. These experimental observations may eventually find some commercial utilization, but it should be noted that there are other promising leads for reducing blistering of house paints.

Small percentages of tetrabutyl titanate added to 93-005 Black definitely improves the wrinkle resistance. This lead is still under active study.

Action

(1) F. & F.'s experimental work with the titanium organics, as outlined above, was reviewed with Messrs. Seidel, Haslam and Brill of the Pigments Department on October 2 at Marshall Laboratory.

(2) At the October 2 meeting, Dr. Brill was requested to give us, in writing, his best recommendations for overcoming the moisture sensitivity of tetraisopropyl titanate, so that this material can be used in a practical way as an adhesion improving agent. J. P. Sermattei will test these suggestions when they are received.

(3) Following his encouraging initial results, R. J. Sheppard will establish the utility of TPT for improving the adhesion of OA topcoat to automotive undercoats.

(4) The use of TPT and TBT as insolubilizers or fast setting agents for nitrocellulose, alkyds, epons, etc., utilizing a double nozzle spray gun for mixing the materials, is being explored by S. Hochberg.

(5) S. Hochberg also plans to prepare a titanated silicone in an effort to produce a silicone polymer which can be cured at lower temperatures.

(6) R. A. LaBerge will include the titanium acylates in his future studies aimed at reducing blistering of outdoor house paints.

(7) No other work with the titanium organics is planned, unless new ideas arise or are suggested by the Pigments Department.

Discussion:

Chemistry of the Titanium Organics

The Titanium Esters

The titanium esters $Ti(OR)_4$ are characterized by rapid hydrolysis on exposure to water or moist air. The rate of hydrolysis varies with the size of the R group, but if R is small (4 carbon atoms or less), hydrolysis is extremely rapid. The end product of the hydrolysis is TiO_2, but the reaction proceeds in steps, and products such as:

$$(RO)_3\,TiO\,Ti\,(OR)_3,\quad R\left[-\begin{matrix}OR\\ OTi\\ OR\end{matrix}-\right]_x OR$$

can also be obtained.

Another reaction of the titanium esters is ester interchange with alcohols. This proceeds rapidly at ordinary temperatures without catalyst. This reaction may be represented by the equation:

$$Ti(OR)_4 + 4R'OH \qquad Ti(OR')_4 + 4ROH$$

It is usually easy to convert a titanium ester to a higher ester by distillation of the lower boiling ROH. Because of this reaction, the titanium esters can be used to crosslink polymers containing hydroxyl groups, such as nitrocellulose, polyvinyl butyral, epon resins and certain alkyds. These reactions are very rapid even at room temperature.

The lower titanium esters are liquids that are soluble in alcohol, hexane and carbon tetrachloride. Tetraisopropyl titanate boils at 232°C.

Dilute solutions of TPT or TBT (5% or less) applied as a thin film to a surface will hydrolyze to give a clear, continuous film, provided the relative humidity is below 40%. At relative humidities higher than 40%, discontinuous or powdery deposits are obtained. Even at low relative humidities, the films are extremely brittle and will craze or powder unless the film thickness is of the order of .1 mil or less.

The Titanium Acylates

The titanium acylates are polymeric materials that have the general formula:

$$R'O\left[\begin{array}{c} O_2CR \\ | \\ -\ TiO\ - \\ | \\ OR' \end{array}\right]_x R' \qquad \text{or} \qquad HO\left[\begin{array}{c} O_2CR \\ | \\ -\ TiO\ - \\ | \\ OH \end{array}\right]_x H$$

Among those that have been prepared are titanium stearate, titanium soy acylate, titanium linseed acylate, titanium castor acylate and titanium cocoanut acylate. These materials range from gummy to waxy solids, which soften and flow at temperatures below 125°C. They are very soluble in non-polar solvents such as hydrocarbons and carbon tetrachloride, and are completely insoluble in polar solvents, such as water and acetone. Unlike the titanium esters, the titanium acylates are reasonably water stable at room temperature, and alcoholysis only take place slowly at elevated temperatures.

The soya and linseed titanium acylates dry much faster than the corresponding drying oils, but they give soft and very brittle films. The titanium acylates have been recommended as modifiers of alkyds and other coatings and as pigment dispersing agents.

Specific Evaluations:

1. As Agents to Improve Adhesion

Tetraisopropyl titanate, applied from a 1-2% solution in anhydrous isopropyl alcohol, was specifically recommended by Pigments Department for improving the adhesion of Trade Sales paints to old, glossy painted surfaces. This suggestion was first tested in K. C. Lampert's group with inconclusive or negative results. J. P. Sermattei then conducted a careful series of tests over old, glossy alkyd, semi-alkyd and oleoresinous paints, using alkyd, semi-alkyd, and latex paints as topcoats - with and without the TPT treatment. In all, 25 panels were prepared in this program, and a total of 450 tests for adhesion were made over a period of one month. In every case, there was no significant improvement in adhesion as a result of the TPT treatment. These tests were made from August 26 to September 23, 1952 in the air conditioned Marshall Laboratory, in which the summer relative humidity is 45-70%.

After this test program was completed, Pigments Department advised that TPT is not effective in improving adhesion, unless the relative humidity is 40% or less at the time it is applied. Obviously such a product is not satisfactory for Trade Sales use. Pigments Department realizes this now, and are trying to overcome the moisture sensitivity of the TPT by addition of small amounts of linseed oil or other material, to a TPT solution in hexane. Such mixed solutions are effective initially, but lose their effectiveness on aging. Pigments Department are now attempting to improve stability on aging. In the meantime, they are no longer recommending 1-2% TPT in anhydrous isopropanol as a "liquid sandpaper" for Trade Sales use. Since the meeting with Pigments Department on October 2, R. J. Sheppard has just recently obtained very promising initial results with a dilute solution of TPT and OA in toluene, used as a wash coat, to improve the adhesion of OA topcoat to automotive undercoats. This work is being continued.

The titanium esters and acylates have also been tested for improving adhesion in the systems listed below. In this work, the titanium ester (TPT or TBT) as a 1-5% solution in anhydrous isopropanol, was usually used as a wash coat direct to the substrate or between coats of the paint system. The titanium acylates were tested by adding them to the topcoat, to the undercoat, or to both.

(A) OA to undercoat. Work done by R. J. Sheppard. Initial results were negative, but very recent work using a mixed TPT/OA solution in toluene looks promising.

(B) "Duco" furniture finishes. Work done by C. J. Welz. Results negative.

(C) Bookbinding adhesives. Work done by J. L. Evans. TPT was used as a primer for an alkali soluble hot melt. Results negative.

(D) Wet adhesion to wood. Work done by R. W. LaBerge. Results negative.

(E) Refrigerator refinish enamel. Work done by G. D. LaBarre.

In this case, octylene glycyl titanate was applied to the baked refrigerator enamel from a 2% and a 5% solution in hydrocarbon. After a short flash time, the refinish enamel was applied. Results were negative.

2. As Agents to Produce Insolubilization or Fast Set

(A) 50% solution of TBT in xylene, applied over a wet film of RL-484 castor oil alkyd, produced surface hardness in 1 minute at room temperature. However, the film below the surface remained soft and the hardened surface showed cracking and frosting. (Work done by J. P. Sermattei). Nevertheless, this is a technique which might be used to produce a fast setting printing ink, since ink films are normally very thin (about 1 mil). A faster setting printing ink is wanted by such large magazine printers as Curtis, Time, Inc., W. F. Hall and others. Pigments Department intimated that Interchemical were working on this problem, using Epon resins as the ink vehicle and a titanium ester as the fast setting agent. S. Hochberg is investigating the effects of mixing TPT and TBT with nitrocellulose, alkyds and Epons by means of a 2-nozzle spray gun. J. R. Huntsberger has reported that applying tetrabutyl titanate over a nitrocellulose film did not produce insolubilization.

3. As Agents to Reduce Blistering of House Paint

R. W. LaBerge has found that wood impregnated with isopropoxy titanium stearate shows a very marked reduction in rate of water absorption (30% pick-up in 3 months for the treated wood, versus 30% pick-up in 2 hours for the untreated wood). Isopropoxy titanium stearate was the most effective agent for this purpose of the many candidates that were examined. LaBerge has also found that isopropoxy titanium oleate applied as a primer to new wood reduces the blistering of #40 Outside White significantly. LaBerge plans to include the titanium acylates in his future program on the moisture blistering problem.

4. As Constituents of House Paints to Improve Durability Characteristics

Titanium stearate (.5, 1. and 1.2% on the paint), tetrastearyl titanate (1 and 6.% on the paint) and tetraisopropyl titanate (1.7 and 4% on the paint) were added in the amounts shown to #40 Outside White. After 1 year Florida exposure, the test paints showed only a slight reduction in copper screen staining and dirt collection. Tetrastearyl titanate gave the best results. On the adverse side, there was increased yellowing and there are also can stability problems. This work was done by R. LaBerge.

5. As Modifiers of Alkyd Resins

Tetrabutyl titanate, added in ratios ranging from 1/99 to 95/25 (solids basis) to RC-453 soya alkyd, gave a progressive increase in yellowing and brittleness of the alkyd film with increasing TBT content. With the normal amount of cobalt drier, 20% TBT in the soya alkyd reduced the tack-free drying time from 6 to 3 hours, but the film was soft, yellow and definitely less flexible compared to the unmodified RC-453. 10% TBT, under the same conditions, lengthened the drying time slightly. In the absence of cobalt, the TBT/alkyd films at 10/90 and 20/80 ratios (solids basis) were slower drying than the straight RC-453 with the normal amount of cobalt. Ratios of TBT above 10/90 give limited can stability, and ratios above 20/80 give incompatible films. (Above work done by H. G. Stauffer and J. P. Sermattei).

Additions of TBT to RL-484 castor oil alkyd resulted in immediate gelation at concentrations of 5% or higher. (J. P. Sermattei).

Titanium soya acylate, added to RC-453 soya alkyd, showed satisfactory compatibility at ratios of 25/75, 50/50, and 75/25 (solids basis), but the blended films were inferior to the straight alkyd in flexibility, yellowing, hardness and adhesion, the degree of deterioration in these properties increasing with the titanium soya acylate content. 50% or more titanium acylate produces a marked reduction in tack-free drying time, but gives soft, brittle films; lesser amounts were not effective in reducing the drying time of the RC-453 soya alkyd. Can stability of all blends was good at the end of one month. (J. P. Sermattei).

6. As Constituents of "Duco" Furniture Sealers

Tetrabutyl titanate was found to improve the combination of drying speed, hardness and flexibility of a Px- cocoanut oil alkyd furniture sealer, but it also caused bad yellowing and could not be used for this reason. (C. J. Welz).

7. As Agents to Reduce Wrinkling

3/4% TBT on the resin solids, added to 93-005 Black, increases the wrinkling film thickness from 1-1/2 to 3 mils in the sun wrinkle test. This is considered a good lead on the wrinkling problem with 93-005 Black. Can stability and effect of aging in the can on wrinkle performance are now under study. (J. R. Huntsberger and R. J. Kluberton).

8. As Pigment Dispersing Agents

Isopropoxy titanium linseed acylate, isopropoxy titanium stearate and isopropoxy titanium soya acylate were tested as agents to improve the dispersion of Monastral Blue, but were not found effective for this purpose. (W. P. Colio).

9. As Crosslinking Agents for U-F and Polyvinyl Acetate Plywood Adhesives

This work is covered in Parlin Laboratory Report #921, by D. K. Ogg, dated October 31, 1946; title: "Evaluation of Titanating Agents for Crosslinking of Adhesives". The results were negative.

10. Miscellaneous Applications

These are covered in Philadelphia Laboratory Report #978, by J. R. Huntsberger, dated September 2, 1949; title: "Alkyl Titanates". The beneficial effect of tetrabutyl titanate on wrinkling was first observed in this work by Huntsberger. A heat resistant, aluminum pigmented paint based on tetrabutyl titanate as the vehicle was developed in this work, but never achieved commercial acceptance. The results otherwise were negative.

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