CC: R. B. Davis, Lab.
Russell Morgan, Lab.
P. B. Evans, Lab.
Paul Robinson, Lab.
R. B. Holmes, Lab.
S. C. Horning, Lab.
S. C. Hochberg, Lab.
L. P. Hubbuch, Lab.
D. L. Herndon, Lab.
R. W. LaBerge, Lab.
J. H. Lowell, Lab.
A. C. Buck, Lab.
H. G. Stauffer, Lab.
W. D. Lawson, Lab.
S. L. Godshalk, Lab.
K. C. Lampert, Lab.
W. A. Hall, Lab.
R. L. Selby, Lab.
C. F. Blaich, Lab.
H. R. Young, Wilm. F&F
O. H. Bullitt, Exp. Sta.
Patent Section, Lab.
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Marshall Laboratory
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MEMORANDUM REPORT NO. M-712:

PREPARED BY: H. E. EASTLACK

ORGANIC TITANATES
MEETING WITH PIGMENTS DEPARTMENT

Introduction:

Following a visit by the writer with G. R. Seidel and John H. Haslam at the Experimental Station on June 14, they, along with W. W. Riches and W. G. Armstrong, also of the Pigments Department, visited the Marshall Laboratory on June 24, to bring us up to date on their work on organic titanium derivatives.

Summary:

Pigments Department research during the past nine months has led to some progress along lines of interest to F.&F. A number of new organic titanium compounds have been prepared and characterized with respect to potential uses.

Action:

A number of samples have been requested for evaluation in various Marshall Laboratory research and sales development programs, as indicated in the detailed discussion below.

DISCUSSION

Blister Resistance of House Paints:

To try to find out why the initial improvement in blister resistance obtained with isopropoxy titanium stearate (TRSTA) disappears after exposure, and in an endeavor to locate compounds which would have a more lasting effect, the Pigments Department has prepared panels treated, before painting, with the following materials:

1.	TRSTA -	isopropoxy titanium stearate
2.	TLNA -	hydroxy titanium linseedate
3.	TTLA -	" " tallate
4.	1190-85 -	distearyl titanium distearyl acetoacetate.
5.	1190-87 -	TRSTA reacted with stearyl lactoacetate (1 mole each)
6.	1190-88 -	diisopropoxy titanium distearyl acetoacetate
7.	TRLNA -	isopropoxy titanium linseedate
8.	TRTLA -	" " tallate
9.	TST -	tetrastearyl titanate
10.	OGTS -	octylene glycyl titanium stearate

After two months exposure, the above panels have been turned over to R. W. LaBerge for blister tests. Duplicates will be available for similar tests after twelve months exposure.

Masonry Sealer:

F.&F. Sales is planning a field test on titanate and silicone masonry sealers. Isopropyl titanium stearate (TRSTA), on which the Pigments Department has the most background, will be the principal titanium organic to be tested, but two others, which they believe may turn out to be more stable, will be included. These are (a) octylene glycyl titanium stearate and (b) TRSTA/diphenyl silanediol copolymer. Samples of each of these materials are being supplied to K. C. Lampert.

In Pigments Department tests, TRSTA still shows good water-proofing after nine months exposure. Although some chalking has occurred and the surface is easily wet, the effectiveness against water penetration is still equal to that obtained with silicones. One concern that is marketing silicone masonry sealers has reported non-uniform behavior (of silicones) and is very much interested in the titanates.

The advantages claimed for titanates in comparison with silicones are (a) lower cost, and (b) windows and trim do not have to be masked to avoid poor adhesion when subsequently painted. However, P. B. Evans pointed out that the wet adhesion

of paint to titanium treated wood is poor. R. W. LaBerge is to check this point on the panels prepared by the Pigments Department for blister resistance tests.

High Temperature Paints:

G. Winter (Australia) has published an article in the December 1953 issue of the Journal of the Oil and Colour Chemist's Association relative to the formulation and performance of polymeric butyl titanate paints using some granular pigments (TiO_2, chrome green, etc.) as well as flake pigments such as Al, Zn, Cu, and mica. The use of mica with TiO_2 gives better results and permits the application of heavier films with good ahesion. In tests on chimney stacks, locomotive fire doors, heaters, and automobile mufflers and motor cylinder heads, butyl titanate paints have out-performed the best previous systems.

Plaskon is reportedly pushing a high temperature paint based on silicone pigmented with aluminum. There may be a market for uses for which no paint has previously been available.

The Pigment Department can readily furnish butyl titanate polymers for use in formulating paints along the lines described by Winter.

Adhesion Promoters:

To successfully use titanium esters as adhesion promoters, premature hydrolysis must be avoided, but hydrolysis must ultimately be complete. The rate of hydrolysis can be controlled by the addition of a small amount of material of low volatility, such as naphthalene. An additive compatible with the topcoat improves the adhesion of the latter to the titanate film. A component of the topcoat is frequently used for this purpose. Tetraoleyl titanate (TOLT) is suggested as the additive for certain purposes.

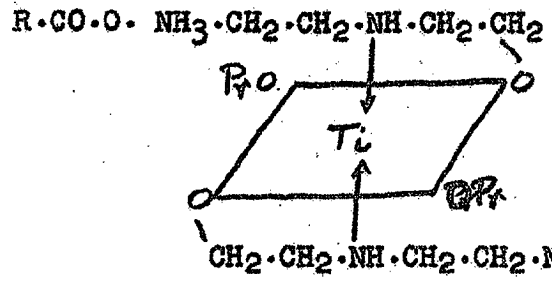
Tetraisopropyl titanate (TPT) is recommended for most uses as an adhesion promoter. However, water soluble titanium chelates, such as triethanol amine titanate, titanium glycollate, and titanium lactate are suggested for certain uses. The latter is said to be an excellent adhesion promoter for styrene-butadiene latex paints. Formulations and suggested uses of organic titanium adhesion promoters are included in Pigments Department Technical Bulletin No. 3.

W. D. Lawson is to send some panels to W. G. Armstrong to determine whether or not improved adhesion of certain air-dry enamels can be demonstrated. C. F. Blaich requested samples of TPT and TOLT.

Corrosion Inhibitor for Steel:

Pigments has developed a new class of amino titanium chelates which show considerable promise as corrosion inhibitors

for steel. Most promising of these is an oil soluble oleic acid salt of isopropoxy B aminoethyl ethanolamine titanate (ATO):



(R·CO·O- = oleic acid radical; Pr = isopropyl)

A nail dipped in a 1% solution of ATO in mineral oil, allowed to drain, and then half submerged in water shows no rusting after more than four months. With straight mineral oil, bad rusting occurs within a few hours. Outdoor durability has not been determined.

Potential uses that have been suggested include: (a) to protect tools, guns, etc., (2) as a component of wax to protect chrome auto trim, (3) to protect steel castings, sheet and structural steel, (4) to prevent back rusting of auto doors and panels (General Motors is said to be interested), and (5) as an additive to primers and paints to improve corrosion resistance (this has not been investigated).

Samples of ATO are to be sent to S. C. Horning and W. A. Hall for evaluation.

Insolublization of Polyvinyl Alcohol and Acetate:

Titanium lactate (which is water soluble and water stable) is being used to insolublize PVAlc films. Heating to about 80°C. is necessary to open up the chelate ring and bring about cross-linking. It should also be effective with partially hydrolyzed PVAc.

Titantium acetonyl acetonate will do the same thing at room temperature, probably through the volatilization of acetonyl acetone. Titanium acetonyl acetonate is a fairly deep yellow; in hydrolyzed product is a pale lemon yellow.

C. F. Blaich requested samples of both titanium lactate and acetonyl acetate.

Ester Exchange Catalysts:

Titanium esters (particularly TPT) are excellent ester exchange catalysts for alcohol ester reactions or reactions between two esters. They cannot be used for esterification reactions because of the water formed.

Orchem is using TPT in making Daktose from methyl methacrylate by ester interchange. It is by far the best catalyst they have tried. Textile Fibers have gotten good results using TPT in making "Dacron" acrylic fiber, except for the yellow color produced. It was stated that yellowing does not occur in reactions carried out at low temperatures and that in any case the intensity is not such as to be objectionable for some paint purposes.

Wood Preservative:

Pentachlorophenoxy titanate has been found (Grasselli tests) to be much more effective as a wood preservative than pentachlorophenol alone, and four times as good as "Wood-Tox". Pentachlorophenoxy titanate is insoluble in hydrocarbons but is solubilized by a mixture with TRSTA. P. B. Evans requested a sample of such a solution for evaluation in C. J. Welz's program on exterior clear finishes for wood.

Other Metal-Organic Derivatives:

The Pigments Department has research under way on organic derivatives of antimony, zirconium, and aluminum. Present effort is concentrated on the chemistry involved, rather than evaluation for end uses. Some samples are available, however, for evaluation within the Company. Russell Morgan requested a few such samples just to have them handy.

Zirconium compound are not degraded by U.V. light (differing from titanium), are more highly colored, and more expensive than titanium, but otherwise appear to have rather similar properties. The characteristics of aluminum compounds appear to be quite different from the titanium analogues. Also, aluminum stearate prepared in anhydrous systems is quite different from the ordinary product prepared in aqueous media. Work on compounds of antimony is just starting.

H. E. Eastlack

H. E. EASTLACK

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