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NATIONAL LEAD'S RESEARCH ON TITANIUM ORGANICS

The writer attended the Gordon conference on Organic Coatings at which two papers were presented by representatives from National Lead Company. It is apparent that they have done considerable work and that we have real competition from them in this field. In order to acquaint our staff with their work, the writer took extensive notes on both talks and is incorporating in this letter the major points. Dr. D. F. Herman gave a talk entitled, "The Chemistry of Titanium Organic Compounds." Dr. Herman is the man who first isolated a compound containing a titanium carbon bond but his talk was principally about titanium esters. In private conversation Dr. Herman said that the Ti-C compounds which he had made so far were all too unstable to have practical use. He described several complexes between butyl titanate and ethylene diamine, ammonia, and HCl and stated that these compounds were somewhat less reactive than the simple esters. He also described association of titanium esters which followed closely our concept of this.

He described four reactions of titanium esters. Reaction with hydrochloric acid was stated to proceed as follows: $Ti(OBu)_4 + HCl$ $(BuO)_3$ TiCl + BuOH.

The hydrolysis of TBT was stated to proceed rapidly but did not go to completion. The following table was given to show the extent of hydrolysis:

Moles TBT/H_2O	Moles H_2O Unreacted	RO per Titanium Remaining
1/.75	.00	2.35
1/1	.02	1.95
1/1.5	.32	1.2
1/1.5	.42	0.96
1/2.0	1.1	0.95 0.85

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As an indication of difference in hydrolysis rates, Lumetron readings were made on solutions of various titanium esters with water added and these are given in Figure 1 attached in the appendix. As expected, the lower titanates hydrolyze much faster than do the higher ones. The hydrolysis of mixed titanates was stated to proceed as expected, the lower boiling alcohol being removed first. Thus, the reaction of dibutyl, dioctyl titanate and 1 mole water would produce condensed dioctyl titanate and 2 moles of butanol.

The reaction with polyols was described briefly and it was stated that depending upon the proportion of TBT to polyol, materials ranging from fluids, to putties, to solids could be produced.

An interesting table was given on the reaction of triethanol amine with TBT in which the butanol was stripped off on a steam bath under vacuum. These results were as follows:

Mole Ratio TEA-TBT	BuO Replaced	Appearance	Water Solubility
0.66	1.96	Very viscous	Partly soluble
1	2.76	Semi solid	Partly soluble
1.33	3.68	Glassy	Soluble
1.5	4.0	Glassy	Soluble

The acylation reaction was described with results analogous to our work. An interesting concept of the mechanism involved was presented, however, in which it was postulated that the mechanism with acetic acid, for example, is as follows:

$$(BuO)_4\ Ti + HOAc \longrightarrow (BuO)_3\ Ti\ (OAc) + BuOH$$

$$BuOH + HOAc \longrightarrow BuOAc + H_2O$$

$$(BuO)_3\ Ti\ (OAc) + H_2O \longrightarrow \left[\begin{array}{c} OAc \\ | \\ -Ti O- \\ | \\ OBu \end{array}\right]_x + 2BuOH$$

As proof of this mechanism Dr. Herman stated that they had actually been able to distill off some water from the reaction mixture.

Although National Lead did not talk much about the acylates, they rather obviously are receiving considerable attention. They have made titanium methacrylate (which we have failed to do) and stated that it polymerized by a normal free radical mechanism.

In private conversation with the writer Dr. Herman stated that National Lead has a new process for producing titanium esters. This involves reaction of $TiCl_4$ with alcohol in a liquid ammonia medium. The co-product ammonium chloride is soluble in liquid ammonia and the reaction mixture separates as two liquid layers, the lower layer being TBT. These are merely separated and the TBT distilled. This has the advantage over our process or avoiding the use of large quantities of solvents and may be more economical.

Dr. H. H. Beacham gave a paper on the use of titanium organic compounds in coatings. He gave numerous examples including many viscosity curves on dopes made from TBT and ethyl cellulose, nitrocellulose, cellulose acetate, alkyds, phenolics, and epoxy resins. He also stated that they had worked with vinyl acetate, vinyl acetate-chloride, vinyl maleates, vinyl ethers, urea-formaldehyde, melamine-formaldehyde, and silicones. In order to minimize gel formation they have used a number of tricks, one of which is the use of butanol as a solvent which tends to reverse the reaction (if TBT is used). Figure 2 shows a graph on this effect with ethyl cellulose. The effect of various alcohols as co-solvents was also described. This is also the system with ethyl cellulose using a fifty-fifty TBT-ethyl cellulose mixture. The solvent was in each case 80% benzene with 20% of various alcohols added. Results were as follows:

Alcohol	Viscosity, cps
MeOH	gel
EtOH	gel
iso-PrOH	p. gel
n-BuOH	275
i-BuOH	300
sec-BuOH	370
t-BuOH	400
ethyl-lactate	225
ethylene glycol	250

It may be seen from this that ethyl lactate and ethylene glycol were more effective in preventing crosslinking than were the simple alcohols. This is to be expected since these materials can form chelates. It should be very useful for us to incorporate such ligands in our cellulose acetate dopes. Amino alcohols and β-diketones as well as simple amines were also used. Figure 3 shows the effect of triethylamine on the viscosity of TBT ethyl cellulose solutions. The effect of ethyl lactate and ethyl acetoacetate on the viscosity of cellulose acetate solutions was given in Figure 4.

The properties of ethyl cellulose and TBT in fifty-fifty mixtures were listed. These showed that the films were harder and more resistant to HCl and various solvents. The material was stated to be water white.

A very hard film was produced from the following formulation:

5 parts of Nitrocellulose
40 parts of Ethyl Lactate
40 parts of Butanol
3 parts of Plasticizing Castor Oil Alkyd
5 parts of Tetra-n-Butyl Titanate (TBT)

In this the plasticizer also reacts and becomes a part of the film. This particular formulation has too low a solid content to be practical.

The following results were obtained by adding TBT to a soy modified alkyd:

	Alkyd	Alkyd + 10% TBT
Color	Yellow	Yellow
Tack-free	24 hrs.	2 hrs.
Hardness		
Air dried 6 days	10	18
H_2O 25° - 6 hrs.	4 (blush)	16
H_2O 100° - 1/2 hrs.	4 (wrinkle)	15
1% NaOH	very soft	10
2 xylol 2 hrs.	very soft	12

With phenolics the following results were obtained:

	Phenolic	Phenolic + 5% TBT
Hardness		
Air dried	15	41
Mineral spirits	dissolved	15
0.5% NaOH	badly swollen	26
Dielectric Strength	1500	2400

Figure 5 shows the effect of triethanol amine titanate added to phenolics on the dielectric strength of the coating.

With epoxy resins it was stated that these materials were difficult to prevent from gelling but that this could be done with β-diketones, triethanol amine, or diamine-TBT complexes. Since diamines are normally added to epoxy resins as a curing catalyst, these were particularly attractive. The formulation which they reported to be good was as follows:

100 parts of Epon 1007
100 parts of Diacetone Alcohol
100 parts of Ethyl Cellosolve
2.5 parts of TBT
2.5 parts of β-amino Ethyl Ethanol Amine

Another formulation was made up in two parts which were merely mixed prior to application. These were as follows:

Part A.

100 parts of Epon 1007

100 parts of Diacetone Alcohol

100 parts of Ethyl Cellosolve

Part B.

6.5 parts of TBT

46.3 parts of Butanol

6.5 parts of Ethylene Diamine

These two solutions were mixed just before curing and cured at 80°C. The resulting films were hard and solvent resistant.

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Appendix

Figure 1

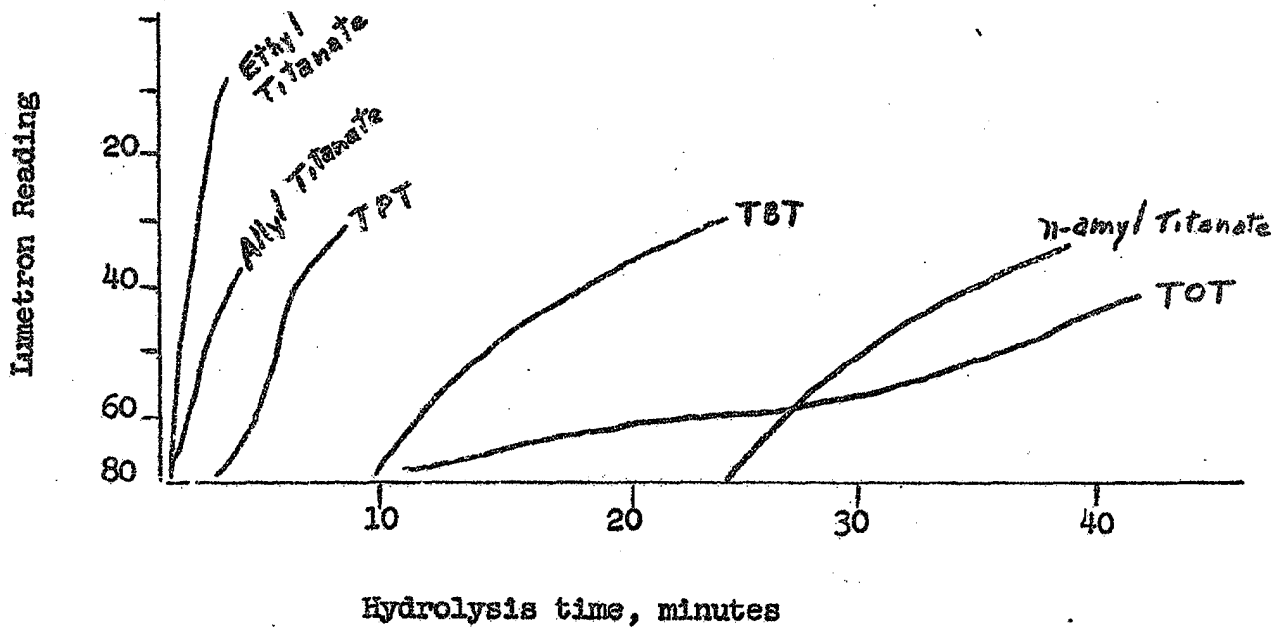

Figure 2

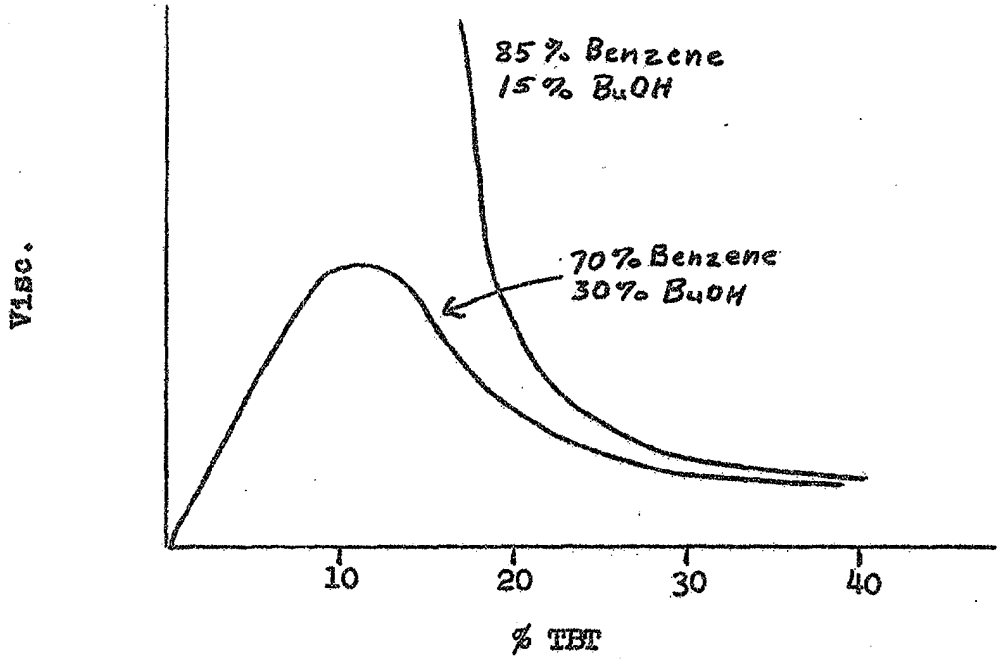

Figure 3

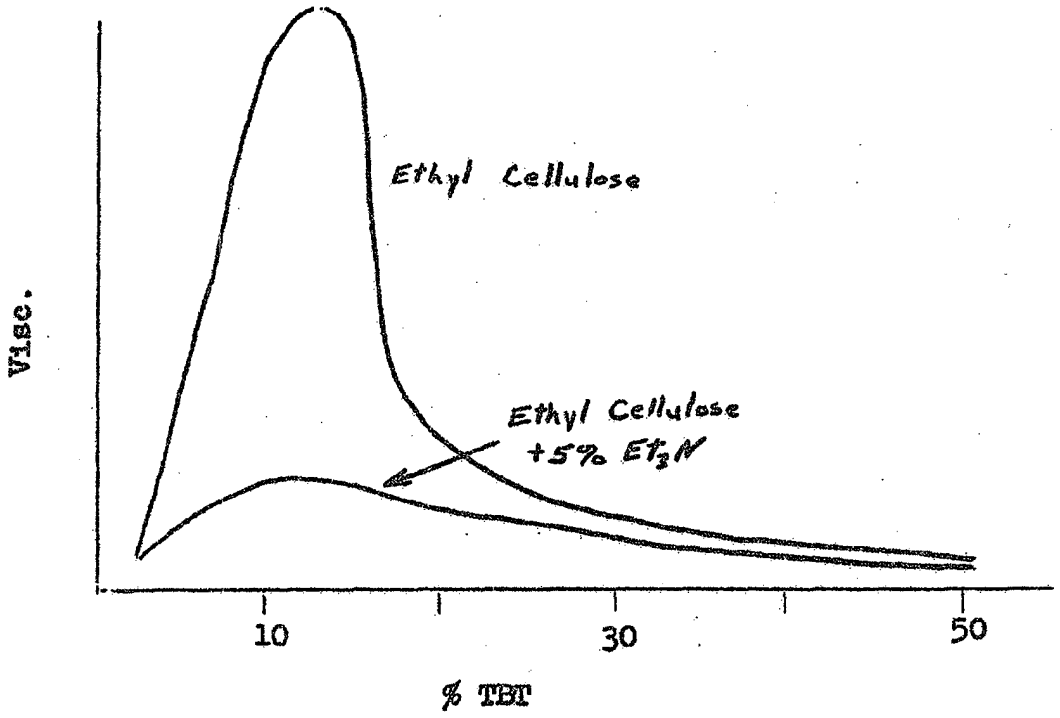

Figure 4

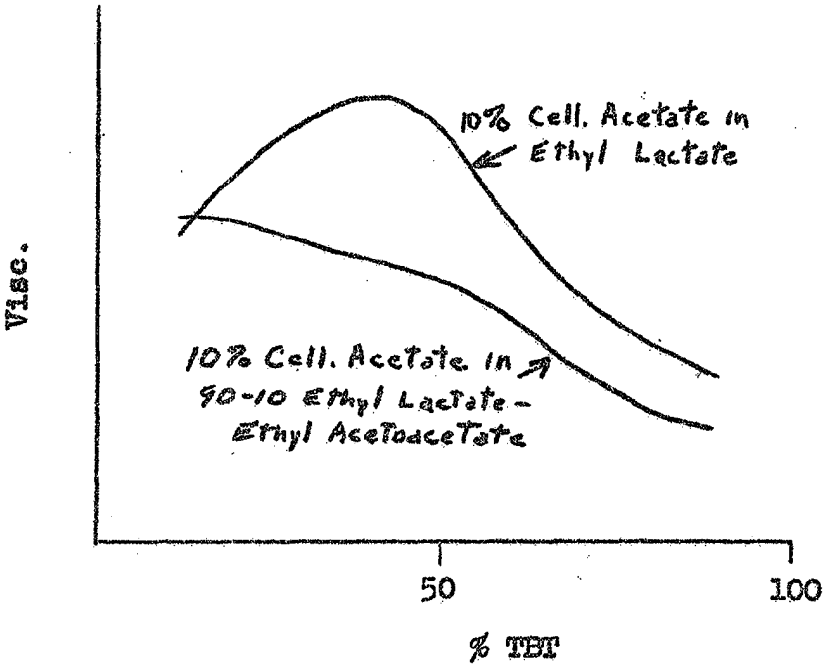

Figure 5