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Preparation and Properties of Esters of Polyorthotitanic Acid*

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INTRODUCTION

The reactions of titanium tetrachloride with aliphatic and aromatic alcohols in the presence or absence of basic neutralizing agents such as sodium, ammonia, amines, and sodium alkoxides have been studied by many investigators.[1-23] This paper reports the results of experimental work designed to clarify the confusion arising from earlier publications on the preparation of esters of orthotitanic acid, $Ti(OR)_4$, and describes the preparation and properties of some esters of polyorthotitanic acid.

DISCUSSION

Nelles[7-10] has reported that when mixtures of titanium tetrachloride and anhydrous aliphatic or aromatic alcohols are treated with ammonia or an aliphatic or aromatic amine, the corresponding tetraesters of orthotitanic acid are produced in good yields (87% for tetraethyl orthotitanate and 80% for tetrabutyl orthotitanate). Kraitzer *et al.*[16] have reported completely successful results from the use of Nelles' method. On the other hand, Speer[21] reports uniformly unsuccessful results in attempts to repeat the examples of Nelles' patents.[7-10] In this laboratory, it was found awkward to repeat exactly the examples in Nelles' patents largely because the reaction mixture became a thick paste difficult to handle conveniently in laboratory glassware. Yields of tetraester of orthotitanic acid which checked substantially Nelles' values were obtained if the paste was extracted with an anhydrous solvent such as benzene, toluene, carbon tetrachloride, etc., or the corresponding alcohol and the solvent extracts were distilled to recover the product. The crude alkyl orthotitanate was purified by rectification at 1 to 2 mm. Hg pressure absolute. Kraitzer[16] has reported successful use of Nelles' procedure when he used a large excess of anhydrous butanol as a medium for the reaction. It has been found most advantageous in this work to use an anhydrous solvent such as toluene, benzene, or carbon tetrachloride as the reaction medium. In such a man-

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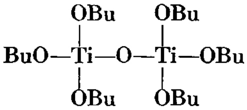
ner, the formation of gross amounts of nonvolatile residues was avoided. The boiling points of the orthotitanate esters checked those reported in the literature, and the titanium dioxide content checked theory.

Several investigators[17–25] have suggested that the esters of orthotitanic acid form polymers which they describe as "condensed titanates." Kraitzer[17] reported that continued heating of butyl titanate results in the loss of volatile material and the formation of "condensed titanates." Winter[23] clarifies this thermal condensation of butyl titanate somewhat by identifying the volatile materials as butanol and butene and states that organic acids accelerate the reaction at lower temperatures. Winter represents the condensed titanate as:



$$\mathrm{BuO{-}\underset{OBu}{\overset{OBu}{Ti}}{-}O{-}\underset{OBu}{\overset{OBu}{Ti}}{-}OBu}$$

He points out further that a process has been developed employing water as the condensing agent and that the polymerized esters derived from butyl titanate contain 41.6 to 50% titanium dioxide. Butyl titanate contains 23.4% titanium dioxide. The condensed titanates vary in appearance from very viscous liquids to semisolids. No further details of the condensation process are reported.

It was discovered previous to Winter's[23] publication that esters of orthotitanic acid can be polymerized to esters of polyorthotitanic acid of known weight-average molecular weight by the cautious addition of water under controlled conditions to solutions of alkyl orthotitanates. The water can be introduced by drawing a fine stream of moist air through a solution of the alkyl orthotitanate dissolved in an anhydrous solvent such as the corresponding alcohol, benzene, toluene, carbon tetrachloride, etc. or by adding a solution of water in the corresponding alcohol to the alkyl orthotitanate dissolved in an anhydrous solvent miscible with that alcohol. Polymers were derived from butyl orthotitanate which contained as much as 56% TiO_2 yet were soluble in such solvents as benzene, toluene, carbon tetrachloride, or butyl alcohol. Since the reactivity of the higher alkyl titanates with water is slower, it is preferred that the polymers of the higher alkyl orthotitanates be prepared by an ester interchange reaction of the higher alcohol with the polymers of the lower alkyl orthotitanates. For example, the octyl or stearyl esters of polyorthotitanic acid are prepared most satisfactorily by heating butyl polyorthotitanate with octyl alcohol or stearyl alcohol and removing the butyl alcohol formed in the ester interchange reaction by distillation under reduced pressure. This reaction is substantially quantitative. Moreover, this ester interchange reaction makes possible the synthesis of mixed esters thus permitting variation in properties of the polyorthotitanate esters by varying the length of the titanium-oxygen chain and by varying the number and the size of the alkyl groups.

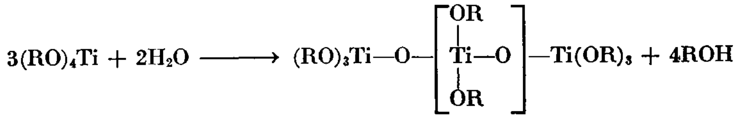
Mixed anhydrides or mixed ester-anhydrides can be formed by replacing the alkyl groups stepwise with an acyl group. This reaction is substantially quantitative. It is preferred that the organic acid be a long-chain fatty acid such as capric, lauric, myristic, stearic, etc. acid. These mixed anhydrides of polyorthotitanic acids and long-chain fatty acids or mixed anhydride-esters are waxy solids soluble in benzene, toluene, carbon tetrachloride, kerosene, etc.

The ease of hydrolysis of the esters of polyorthotitanic acid is much greater than the corresponding ester of orthosilicic acid. In the addition of sufficient water to butyl orthotitanate so that the resulting product may be represented as a dimer, hexabutyl pyrotitanate, no butyl orthotitanate is recovered and the analysis of the product for TiO_2 checks very closely with the theoretical TiO_2 content of the dimer. Furthermore, addition of butyl orthotitanate to a tetramer or decamer, for example, results in a product of lower weight-average molecular weight from which no butyl titanate is recovered. Moreover, when the water–alcohol solution is added at a rapid rate during the condensation reaction transient cloudy streaks are observed where the water–alcohol solution contacts the reaction mixture. This indicates that insoluble three-dimensional polymers are produced which react rapidly with butyl orthotitanate or butyl polyorthotitanate and disappear. No titanium dioxide is formed unless the water is added too rapidly from a more concentrated solution in alcohol. This resolution of three-dimensional polyorthotitanate esters proceeds very rapidly even at room temperature.

To calculate the quantity of water required to cause a certain degree of polymerization, consider the following equations:

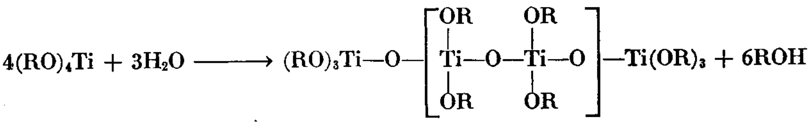
(I) $2(\mathrm{RO})_4\mathrm{Ti} + \mathrm{H_2O} \longrightarrow (\mathrm{RO})_3\mathrm{Ti{-}O{-}Ti(OR)_3} + 2\mathrm{ROH}$

(II)



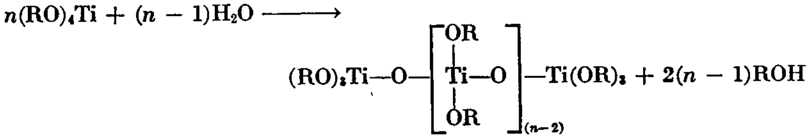
$$3(\mathrm{RO})_4\mathrm{Ti} + 2\mathrm{H_2O} \longrightarrow (\mathrm{RO})_3\mathrm{Ti{-}O{-}}\left[\begin{array}{c}\mathrm{OR}\\ |\\ \mathrm{Ti{-}O}\\ |\\ \mathrm{OR}\end{array}\right]\mathrm{{-}Ti(OR)_3} + 4\mathrm{ROH}$$

(III)



$$4(\mathrm{RO})_4\mathrm{Ti} + 3\mathrm{H_2O} \longrightarrow (\mathrm{RO})_3\mathrm{Ti{-}O{-}}\left[\begin{array}{ccc}\mathrm{OR} & & \mathrm{OR}\\ | & & |\\ \mathrm{Ti} & \mathrm{{-}O{-}} & \mathrm{Ti{-}O}\\ | & & |\\ \mathrm{OR} & & \mathrm{OR}\end{array}\right]\mathrm{{-}Ti(OR)_3} + 6\mathrm{ROH}$$

(IV)



$$n(\mathrm{RO})_4\mathrm{Ti} + (n-1)\mathrm{H_2O} \longrightarrow (\mathrm{RO})_3\mathrm{Ti{-}O{-}}\left[\begin{array}{c}\mathrm{OR}\\ |\\ \mathrm{Ti{-}O}\\ |\\ \mathrm{OR}\end{array}\right]_{(n-2)}\mathrm{{-}Ti(OR)_3} + 2(n-1)\mathrm{ROH}$$

It is seen that the number of moles of water required per mol of $(\mathrm{RO})_4\mathrm{Ti}$ to cause a degree (n) of polymerization is given by the equation:

$$\text{moles of water for } n \text{ DP} = (n - 1)/n$$

where n is the degree of polymerization and the number of monomer units in the polymer. When n approaches infinity:

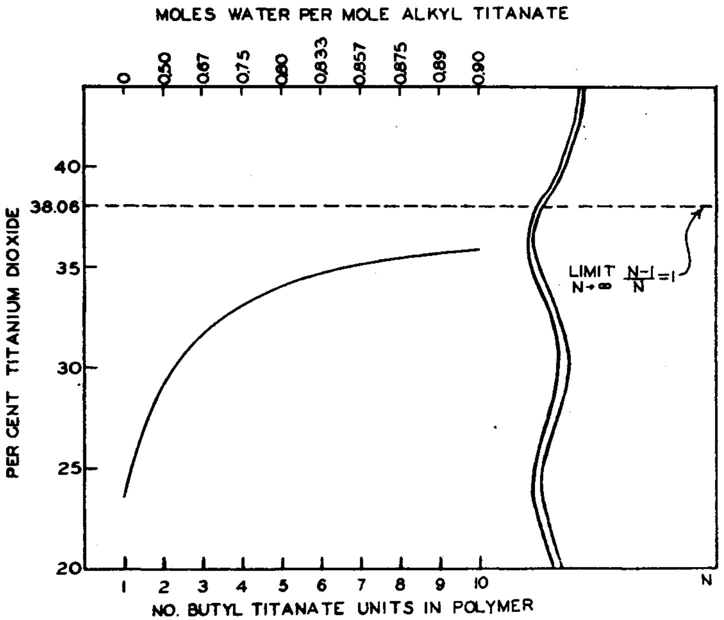


Fig. 1. Per cent titanium dioxide in butyl polyorthotitanate as a function of degree of polymerization.

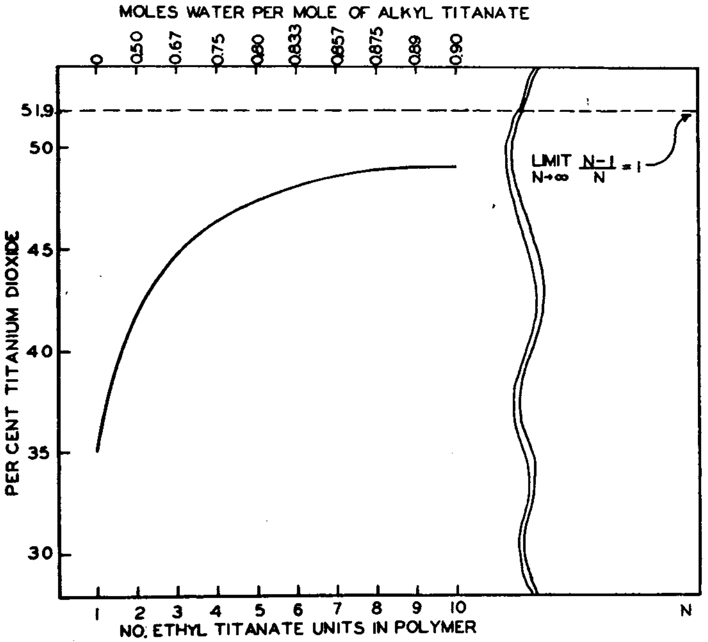
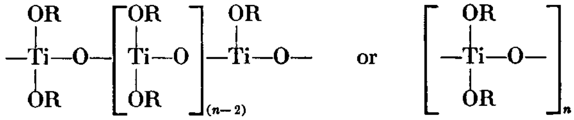


Fig. 2. Per cent titanium dioxide in ethyl polyorthotitanate as a function of degree of polymerization.

$$\operatorname*{limit}_{n\to\infty} \frac{n-1}{n} = 1$$

This is interpreted to mean that, in the equilibrium state, if the mole ratio of water to alkyl orthotitanate is less than 1, there should be substantially no cross-linked polymer in the resin, although there may be considerable chain branching in the polymer molecule. In the limit, $n \to \infty$, the polymer molecule may be represented as:



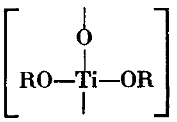
$$-\underset{OR}{\overset{OR}{\overset{|}{\underset{|}{Ti}}}}-O-\left[\underset{OR}{\overset{OR}{\overset{|}{\underset{|}{Ti}}}}-O\right]_{(n-2)}-\underset{OR}{\overset{OR}{\overset{|}{\underset{|}{Ti}}}}-O- \quad \text{or} \quad \left[-\underset{OR}{\overset{OR}{\overset{|}{\underset{|}{Ti}}}}-O-\right]_n$$

In Figure 1, the per cent TiO_2 as a function of polymerization degree has been plotted for butyl titanate. Also:

$$\operatorname*{limit}_{n\to\infty} \frac{n-1}{n} = 1$$

has been shown. Similarly, Figure 2 represents the same relationships for ethyl titanate. The experimental agreement with Figures 1 and 2 is very close up to a polymerization degree of 6. The difference in TiO_2 content of polymers having a polymerization degree exceeding 6 is smaller than the experimental error in determining the TiO_2 content in the polymers. The discrepancy between the experimentally sought and the experimentally derived polymerization degree has not exceeded 0.2 unit.

Consider next the question of cross-linking. Cross-linking should proceed by the interaction of:



$$\left[\begin{array}{c} | \\ O \\ | \\ RO-Ti-OR \\ | \end{array}\right]$$

groups with water. Following the same logic as before for the uncross-linked polymers, one might expect that the amount of water required for the cross-linking reaction per mole of available titanium can be expressed by the equation:

$$\text{moles of water for } m \text{ degree of cross-linking} = (m-1)/m$$

When m approaches infinity and:

$$\operatorname*{limit}_{m\to\infty} \frac{m-1}{m} = 1$$

all of the ester groups are hydrolyzed. Therefore, when one mole of orthotitanate has been hydrolyzed, one mole of water will be required to form a linear polymer of infinite DP and an additional mole of water will be required to hydrolyze the polymer to TiO_2. This is essentially what happens slowly when films of condensed titanates are exposed to the atmosphere. The initial film is transparent, but, in time, it becomes opaque and brittle.

In a series of experiments (Table I) where the mole ratio of H_2O to Ti exceeded 1, the condensation reaction behaved quite differently than was expected in

$$\lim_{m \to \infty} \frac{m-1}{m} = 1$$

TABLE I

EFFECT OF WATER ON CONDENSATION POLYMERIZATION OF BUTYL ORTHOTITANATE

Expt.	H_2O Added, g.	H_2O Recovered, ml.	H_2O/Ti, moles/mole Added	H_2O/Ti, moles/mole Recovered	H_2O/Ti, moles/mole Consumed	TiO_2 in product, %
1	4.31	0	1.20	0	1.20	—
2	5.40	0.2	1.50	0.05	1.45	51–52
3	5.84	0.5	1.62	0.14	1.48	53.4
4	6.30	1.0	1.75	0.28	1.47	55
5	7.20	1.7	2.00	0.47	1.53	56
6	8.12	2.4	2.25	0.67	1.58	—

Water was recovered from the polymerization mixture. It appears from Table I that, below a ratio of $H_2O/Ti = 2.25$, roughly 1.4–1.5 moles of water are consumed per mole of titanium. When the ratio of H_2O/Ti is 3, TiO_2 precipitates. The TiO_2 content of the products increased progressively from 51 to 56%. All were soluble in toluene, benzene, carbon tetrachloride, or butyl alcohol. Further study of this condensation is necessary. It would appear that, to a limited extent, the condensation reaction is an equilibrium reaction, and that the ease of hydrolysis of butoxy groups becomes progressively more difficult as the degree of polymerization increases. Gels have been derived by allowing solutions of alkyl titanates to stand exposed to the atmosphere, but the gels have not been produced under controlled experimental conditions.

Exploratory study of the number average molecular weight of the alkyl polyorthotitanates by cryoscopic measurements on benzene solutions has brought out some abnormally high results. Further study of the problem is required.

EXPERIMENTAL

Preparation of Butyl Orthotitanate

To a two-liter three-necked round bottom flask fitted with an electrically driven stirrer, a 100 ml. dropping funnel, a thermometer, and a vent tube connected to a calcium chloride drying tube and immersed in an ice bath were added 900 ml. of toluene dried over sodium and 156 g. of freshly distilled anhydrous 1-butanol. When the resulting mixture had cooled to 10°C., 100 g. redistilled C.P. titanium tetrachloride was added dropwise as rapidly as possible while the temperature of the flask contents was kept between 10 and 15°C. About 15 minutes were required to add the titanium tetrachloride. Stirring was continued for about an hour; then anhydrous ammonia was bubbled into the reaction mixture until it was alkaline. The reaction mixture, which had become a thick slurry, was transferred to four 250 ml. centrifuge bottles and centrifuged until the supernatant liquid was clear. The supernatant liquid was decanted, and the ammonium chloride residue was washed by redispersing it in 100 ml. of dry toluene and recentrifuging the slurry. The supernatant liquid was decanted and added to the first liquid decanted. The ammonium chloride was washed three additional times with 100 ml. portions of dry toluene. The combined washings and butyl orthotitanate solution were distilled in a rectifying column first at atmospheric pressure until no distillate was recovered when the still pot contents were at 150°C. Distillation was continued under progressively reduced pressure to complete the removal of solvent. The butyl orthotitanate remaining was distilled at 152–154°C. at 1 mm. Hg absolute pressure. The yield of butyl orthotitanate was 80 to 85% (140–155 g.). The product is a light yellow, viscous liquid possessing a fruity odor.

The product was analyzed for TiO_2 by weighing a sample into a tared crucible, adding about 1 ml. of 1% nitric acid, evaporating the water in an oven at 70–75°C., and heating the crucible for 2 hours in a muffle furnace at 1200°C. Per cent TiO_2 found was 23.30 ± 0.04 (calculated 23.48).

Preparation of Ethyl Titanate

The same apparatus and procedure as were used in the preparation of butyl titanate were employed except that 97 g. of 200 proof ethanol was added to 900 ml. of dry toluene. The yield of ethyl titanate was 80 to 85%. The product boiled at 112°C. at 1 mm. Hg absolute pressure.

Preparation of Alkyl Polytitanates

In a 1000 ml. three-necked flask fitted with an electrically driven stirrer, a dropping funnel, and a vent tube fitted with a calcium chloride drying tube, 250 g. of butyl titanate was dissolved in 150 ml. of dry toluene. A solution of 6.63 g. of water in 100 ml. of dry butanol was added dropwise to the stirred butyl orthotitanate solution. When this addition was completed, the contents of the flask were transferred to a 1000 ml. round bottom flask fitted to a distilling column 30 cm. long and 20 mm. in diameter and packed with 7 mm. × 7 mm. Raschig rings. The butanol and toluene were recovered at atmospheric pressure until the temperature of the still pot rose to 160°C. The pressure was reduced gradually to 1 mm. Hg absolute to remove the remaining solvent. The temperature of the still pot was allowed to rise to 200°C. where it was kept for 30 minutes. No butyl orthotitanate was recovered. This product had a polymerization degree of 2.1 and a TiO_2 content of 29.3%. The TiO_2 content of hexabutyl pyrotitanate, $Bu_6Ti_2O_7$, is 29.1%. Polymers of greater polymerization degree can be prepared by adding more water.

In a series of experiments where the mole ratio of H_2O to Ti exceeded 1, the condensation reaction behaved differently than expected. Water can be recovered from the polymerization mixture. In the series of experiments tabulated in Table I, 68 g. of butyl orthotitanate dissolved in 100 ml. of dry toluene, was treated with varying amounts of water dissolved in 50 to 75 ml. of dry butanol. The technique employed in adding the water was the same as that used in the preparation of the alkyl polytitanates of low polymerization degree, *i.e.*, 2 to 6. The water was recovered by use of a Dean-Stark Distilling Tube Receiver.

The recovery of unconsumed water becomes more difficult as the amount to be recovered becomes greater. A small amount of water collects as droplets in portions of the still which are difficult to heat above the boiling point of the water–toluene–butanol mixture. These droplets on returning to the boiling solution form TiO_2 beads. The amount of water recovered in the form of TiO_2 was estimated carefully. The amount of water consumed in the condensation reaction does not exceed about 1.4–1.5 moles H_2O per mole Ti. When the mole ratio H_2O/Ti is above 3, all of the titanate is converted to TiO_2. All of the products are soluble in dry toluene. The products derived in experiments 1–3 begin to melt about 120–140°C. and are stable liquids at 200°C. When heated to 250–275°C., they decompose and butyl ether is recovered. Butylene was not recovered as an expected by-product in a dry-ice trap. The products in experiments 4–6 are solids at 200°C. and begin to char above 225°C. in vacuum.

In studies of the synthesis of alkyl titanates from anhydrous butyl alcohol and titanium tetrachloride employing ammonia or an amine to neutralize the hydrogen chloride formed, Speer has reported uniformly unsuccessful results in repeating the examples of Nelles' patents on this process. Kraitzer, Winter, and others followed Nelles' process successfully employing a large excess of anhydrous butyl alcohol. Repetition of Nelles' patent examples is awkward because the ammonium chloride formed in the reaction produces a thick slurry too inconvenient to handle. However, if this slurry was diluted or extracted with an hydrous hydrocarbon solvent, *i.e.*, toluene, yields of 80% were achieved. Furthermore, since it is difficult to obtain rigorously anhydrous alcohols, it is more convenient to carry out the synthesis of alkyl titanates using an inert anhydrous solvent, *i.e.*, toluene or carbon tetrachloride, as a reaction medium along with the stoichiometric quantity of alcohol instead of using a large excess of the alcohol as the reaction medium. The formation of nonvolatile residues was avoided.

If the proper quantity of water dissolved in a low-boiling alcohol is added slowly with stirring to a solution of the corresponding ester of orthotitanic acid, it is possible to obtain esters of polyorthotitanic acid of controlled average molecular weight. If less than 1 mole of water per mole of orthotitanate esters is employed, the amount of cross-linked polymer derived is vanishingly little. When the butylorthotitanate wax treated with 1.5–2.25 moles of water per mole of titanium, 1.4–1.5 moles of water were consumed per mole of titanium. Water was recovered from the system. Water in excess of 2.25–3 moles of water per mole of titanium caused complete conversion of butylorthotitanate to titanium dioxide. The polyorthotitanates were soluble in benzene, toluene, and butyl alcohol. The uncross-linked polymers vary in appearance from very viscous liquids to waxy solids. The polyorthotitanates enter into ester interchange reactions with alcohols in which one to all of the lower boiling alkyl groups may be replaced by the higher one. Long-chain organic acids react with the alkyl polyorthotitanates or the alkyl *titanates to replace one to all of the alkyl groups.*

Preparation of Butyl Stearyl Pyrotitanates

In the preparation of butyl stearyl pyrotitanates, butyl pyrotitanate is mixed with stearyl alcohol, and the mixture is heated slowly to 200°C at 1 mm. Hg absolute pressure. The yield of butyl alcohol recovered in a dry-ice trap is practically theoretical. By prior choice, one to six of the butyl groups may be replaced by stearyl groups. Other alcohols boiling higher than butyl alcohol or phenol may be used similarly. Butyl polytitanates of higher polymerization degree react similarly with higher boiling alcohols and phenols.

Preparation of Butyl Stearoyl Pyrotitanate

Appropriate molar quantities of butyl pyrotitanates and stearic acid are heated under the same conditions as butyl pyrotitanate and stearyl alcohol. The butyl alcohol recovered is practically theoretical. No butyl stearate was isolated.

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Synopsis

In studies of the synthesis of alkyl titanates from anhydrous butyl alcohol and titanium tetrachloride employing ammonia or an amine to neutralize the hydrogen chloride formed, Speer has reported uniformly unsuccessful results in repeating the examples of Nelles' patents on this process. Kraitzer, Winter, and others followed Nelles' process successfully employing a large excess of anhydrous butyl alcohol. Repetition of Nelles' patent examples is awkward because the ammonium chloride formed in the reaction produces a thick slurry too inconvenient to handle. However, if this slurry was diluted or extracted with an anhydrous hydrocarbon solvent, *i.e.*, toluene, yields of 80% were achieved. Furthermore, since it is difficult to obtain rigorously anhydrous alcohols, it is more convenient to carry out the synthesis of alkyl titanates using an inert anhydrous solvent, *i.e.*, toluene or carbon tetrachloride, as a reaction medium along with the stoichiometric quantity of alcohol instead of using a large excess of the alcohol as the reaction medium. The formation of nonvolatile residues was avoided.

If the proper quantity of water dissolved in a low-boiling alcohol is added slowly with stirring to a solution of the corresponding ester of orthotitanic acid, it is possible to obtain esters of polyorthotitanic acid of controlled average molecular weight. If less than 1 mole of water per mole of orthotitanate esters is employed, the amount of cross-linked polymer derived is vanishingly little. When the butylorthotitanate was treated with 1.5–2.25 moles of water per mole of titanium, 1.4–1.5 moles of water were consumed per mole of titanium. Water was recovered from the system. Water in excess of 2.25–3 moles of water per mole of titanium caused complete conversion of butylorthotitanate to titanium dioxide. The polyorthotitanates were soluble in benzene, toluene, and butyl alcohol. The uncross-linked polymers vary in appearance from very viscous liquids to waxy solids. The polyorthotitanates enter into ester interchange reactions with alcohols in which one to all of the lower boiling alkyl groups may be replaced by the higher one. Long-chain organic acids react with the alkyl polyorthotitanates or the alkyl titanates to replace one to all of the alkyl groups.

Résumé

Dans l'étude de la synthèse des titanates d'alcoyle aux dépens d'alcool butylique et de tétrachlorure de titane, en présence d'ammoniaque ou d'une amine en vue de neutraliser l'acide chlorhydrique formé, Speer a rapporté uniformément les résultats négatifs de ses essais en répétant les exemples des brevêts de Nelles suivant ce procédé. Kraitzer Winter et autres suivirent avec succès le procédé de Nelles en utilisant un large excès

d'alcool butylique anhydre. Reproduire les exemples du brevêt de Nelles est delicat à cause du chlorure ammonique formé au cours de la réaction qui entraine la formation d'une masse pâteuse consistante difficile à manipuler. Toutefois, après dilution ou extraction avec un hydrocarbure anhydre comme solvant, tel le toluène, on peut obtenir 80% de rendement. De plus, comme il est difficile d'obtenir des alcools strictement anhydres, il est plus aisé d'effectuer la synthèse des titanates d'alcoyles en utilisant comme milieu de réaction un solvant inerte anhydre, tel le toluène ou le tétrachlorure de carbone. Ceci permet de travailler avec une quantité stoechiométrique d'alcool, au lieu d'en utiliser un large excès, comme milieu de réaction. La formation de résidus nonvolatils est évitée.

Si une quantité appropriée d'eau, dissoute dans un alcool à faible point d'ébullition est ajoutée lentement sans agitation à la solution de l'ester orthotitanique correspondant, on peut obtenir des esters polyorthotitaniques d'un poid moléculaire déterminé. Si on utilise moins d'une mole d'eau par mole d'ester orthotitanique, la quantité de polymère ponté est négligeable. Lorsque l'orthotitanate de butyle est traité par 1.5 à 2.25 moles d'eau par mole de titane, on constate que 1.4–1.5 moles d'eau sont consommées par mole de titane. On recupère de l'eau du système. L'eau en excès de 2.25–3 moles d'eau par mole de titane entraine la transformation complète de l'orthotitanate de butyle en dioxyde de titane. Les polyorthotitanates sont solubles dans le benzène, le toluène et l'alcool butylique. Les polymères non-pontés varient en apparence, de liquides très visqueux à des solides cireux. Les polyorthotitanates participent à des réactions d'échange d'ester avec les alcools; au cours de celles-ci, un groupe alcoyle, parfois tous ces groupes, peuvent être remplacés par des alcools à point d'ébullition plus élevés. Les polyacides organiques réagissent avec les polyorthotitanates d'alcoyle en remplaçant un ou tous les groupes alcoyles.

Zusammenfassung

In Untersuchungen der Synthese von Alkyltitanaten aus wasserfreiem Butylalkohol und Titaniumtetrachlorid unter Benutzung von Ammoniak oder von einem Amin zur Neutralisierung des gebildeten Chlorwasserstoffs hat Speer bei der Nacharbeitung der Beispiele von Nelles' Patenten für diesen Prozess einheitlich erfolglose Resultate berichtet. Kraitzer, Winter und andere wiederholten den Prozess von Nelles erfolgreich, indem sie einen grossen Überschuss an wasserfreiem Butylalkohol verwendeten. Die Nacharbeitung von Nelles' Patentbeispielen ist unbequem, da das während der Reaktion gebildete Ammonium chlorid einen dicken Brei bildet, der schwer zu handhaben ist. Wenn aber dieser Brei verdünnt oder mit einem wasserfreien Kohlenwasserstoff-Lösungs mittel, zum Beispiel Toluol, extrahiert wird, werden Ausbeuten von 80% erhalten. Da es schwierig ist, vollkommen wasserfreie Alkohole zu erhalten, ist es ausserdem bequemer, bei der Synthese von Alkyltitanaten als Reaktionsmedium ein träges, wasserfreies Lösungsmittel wie Toluol oder Tetrachlorkohlenstoff zusammen mit der stöchiometrischen Alkoholmenge zu benutzen, anstatt einen grossen Überschuss an Alkohol als Reaktionsmedium zu verwenden. Die Bildung nicht flüchtiger Rückstände wurde vermieden.

Wenn die entsprechende Menge Wasser, in einem niedrig siedenden Alkohol gelöst, langsam unter Rühren zu einer Lösung des entsprechenden Esters von Orthotitansäure zugefügt wird, ist es möglich, Ester der Polyorthotitansäure von kontrolliertem Durchschnittsmolekulargewicht zu erhalten. Wenn weniger als ein Mol Wasser pro Mol Orthotitanatester verwendet wird, ist die Menge an erhaltenem Querbindungspolymer verschwindend klein. Bei Behandlung des Butylorthotitanates mit 1.5 zu 2.25 Mol Wasser pro Mol Titan wurden 1.4–1.5 Mol Wasser pro Mol Titan verbraucht. Das Wasser wurde aus dem System zurückgewonen. Ein Wasserüberschuss von 2.25–3 Mol Wasser pro Mol Titan bewirkte einen vollständigen Umsatz des Butylorthotitanats zu Titaniumdioxyd. Die Polyorthotitanate waren in Benzol, Toluol und Butylalkohol löslich. Die nicht Querbindungen enthaltenden Polymere variieren äusserlich von sehr viskosen Flüssigkeiten zu wachsartigen festen Körpern. Die Polyorthotitanate gehen Umesterungsreaktionen mit Alkoholen ein, wobei ein bis alle der niedriger siedenden Alkylgruppen durch höhere ersetzt werden können. Langkettige organische Säuren reagieren mit den Alkyl-Polyorthotitanaten, indem sie eine bis alle Alkylgruppen ersetzen.

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