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Synthesis of Alumatrane and It's Application as Gelling Agent in Lithographic Ink Formulations

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Aluminum alkoxides modified with alkanolamines has been used in wide range of applications in industry, such as textile-treating agents, gelling agent in lithographic inks, paints and other coatings. In this work sample of triethanolamine aluminates were prepared from aluminum isopropoxide and aluminum hydroxide and their ability to build up stable gel was examined in lithographic ink formulation and then qualities were compared to commercial samples. All samples were characterized by FT-IR, ^{27}Al NMR, TGA and elemental analysis. For investigation of effect of alkoxide precursor on quality of sol-gel dried alumina, some of prepared alkoxides were hydrolyzed in different conditions. BET of some samples show better surface area, respect to previously reported methods of sol-gel derived alumina.

Key Words: Alumatranes, Triethanolamine, Lithographic ink.

INTRODUCTION

Aluminum compounds have wide range of applications in industrial areas, particularly in catalysis, adsorbents, coating and composites[1].

Atranes (Fig. 1) with M = B, Al, Si, Ge, Sn, Pb, have been synthesized and studied over the last three decades[1]. These compounds are of interest owing to their cage structure and physico-chemical properties.

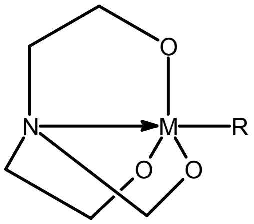


Fig. 1. General formula of atranes

There are several methods of preparing alumatranes. Alumatrane is prepared in high yield by reaction of aluminum alkoxides and alkanolamines in an aromatic solvents[2,3] or without solvent[4-6]. Triethylaluminum also reacts with triethanolamione in toluene or hexane at -78 °C to form alumatrane[7]. Verkade[8] prepared alumatrane by the alcoholysis of *tris*-(dimethylamide) aluminum with triethanolamine. Synthesis of alumatranes directly from the reaction of inexpensive aluminum hydroxide and alkanolamines were reported in a patent but no more information are available[9]. Yukoltron *et al.*[9] also found that high boiling point amines such as diethylenetriamine and triethylenetetramine can be used either in catalytic or stoichiometric quantities to dissolve SiO_2. Moreover, they also found that approximately stochiometric quantities of triethanolamine will effectively[9] dissolve $Al(OH)_3$.

Alumatranes have good solubility in organic solvents such as hydrocarbon solvents. These compounds can be used to prepare organic solutions with a high concentration of aluminum ions. These properties caused that they use as gelling agent in lithographic inks, paints and the other similar formulation.

The purpose of this work is to extend previous effort to reactions of $Al(OH)_3$ with triethanolamine and study of application of prepared compounds in lithographic inks as gelling agent.

EXPERIMENTAL

The starting materials and products are slightly moisture and air sensitive, therefore all reactions were carried out under dry nitrogen atmosphere. Solvents were obtained from Merck and purified and dried before use. Aluminum hydroxide and aluminum isopropoxide were obtained from Aldrich Chemical Co. and were used without further purification. Triethanolamine was obtained from May & Baker.

^{27}Al NMR was recorded on Bruker 300 MHz. Fourier transform infrared spectra were recorded on Tensor 27, Bruker. For viscosity measurement of prepared ink formulations a Fann Viscometer model 35A was used. Specific surface area was obtained by micromeritics ASAP 2020 surface area and porosimetry system.

Synthesis of alumatrane from aluminum isopropoxide: A mixture of 10.2 g (0.05 mol) aluminum isopropoxide, 6.6 mL (0.05 mol) triethanolamine and about 100 mL benzene is refluxed in a three-nacked, round-bottomed flask fitted with stirrer, nitrogen inlet, Dean-stark trap and condenser. Refluxing and distillation are continued until the isopropanol-benzene azeotrope come over.

The solvent was removed by evaporation and the product is recrystallized from benzene-hexane mixture. The white product does not melt below 300 ºC (sample A). This process was repeated in toluene and sample B was synthesized.

Synthesis of alumatrane from aluminum hydroxide: To suspension of 0.05 mol aluminum hydroxide in 100 mL xylene in a two-necked round bottom flask, 0.05 mol triethanolamine was added. The reaction mixture was stirred and heated under nitrogen. Refluxing was continued until the water xylene azeotrop come over. After keeping the reaction mixture stands without stirring over night, white product precipitated out. After filtration, product was stirred with acetonitrile overnight to removes excess of triethanolamine. The solid was then filtered off and dried under vacuum. (Product C). This process was repeated in dioxane and sample D was synthesized.

Gel preparation: Dilute solution of selected samples in isopropanol with stochiometric amount of water was hydrolyzed. Gel dried at 110 ºC and calcined for 4 h in 600 ºC. The specific surface area of obtained alumina was measured by standard gas adsorption method.

RESULTS AND DISCUSSION

Samples A, B, C and D were characterized by FT-IR, ^{27}Al NMR and thermal analysis. The FT-IR spectra of the products show similar functional groups (Table-1). Due to moisture sensitivity of the product O-H stretching appears at 3700-3300 cm^{-1}. The wave number at 3000-2750 cm^{-1} corresponds to OH overton and OH bending.The broad peak at 800-500 cm^{-1} represents the ν(Al-O) and ν(Al-N) vibration.

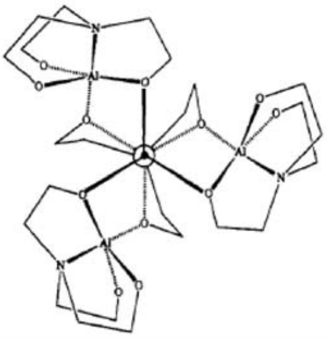
TABLE-1
FT-IR SPECTRA (cm^{-1}) OF PRODUCTS

Bands	Assignments
3700-3300	ν(OH)
3000-2750	ν(OH)
1450	ν(OH)
1200-1000	ν(C-N), δ(OH)
800-500	ν(Al-O), ν(Al-N)

The reports on the ^{27}Al NMR spectroscopy of alumatranes claiming monomeric behaviour for these compounds in chloroform solution and a tetrahedral environment around the central aluminum atom[10]. The present results are in sharp contrast with previous studies.

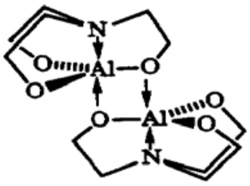
In the ^{27}Al NMR spectrum of alumatrane synthesized from aluminum alkoxide in benzene, sample A, two peaks at 8.5 and 68.9 ppm were observed. The sharp peak at 8.5 ppm belongs to single hexa coordinated aluminum atom, where the signal at 68.9 ppm can be assigned to three equivalent penta coordinated atoms. Al atoms are coordinated by four oxygen and nitrogen atoms[11], while the structural units coordinated by five oxygen atoms show a peak in the range from 30 to 40 ppm. Therefore, coordination of nitrogen instead of oxygen induces about 30 ppm peak shift[11].

These observations are consistent with the presence of tetramer **I** in solution as a major species.



I

For samples C and D one peak at 69.6 and 70 ppm was observed, respectively. This can be assigned as five coordinated aluminum, with dimmeric structure **II**.



II

According to ^{27}Al NMR and FT-IR results alumatrane synthesized from aluminumn isopropoxide is tetrameric in solution while alumatrane synthesized from aluminum hydroxide is a dimer.

For investigation of application of prepared alumatrane in the lithographic inks, selected samples were used as gelling agent in a typical lithographic ink formulation as shown in Table-2.

TABLE-2
COMPOSITION OF A TYPICAL LITHOGRAPHIC INK FORMULATION

Compounds	Amount (%)
Pentalyn resin*	30.0
Alkyd resin**	10.0
Tung oil	5.0
Solvent ***	45.5
Cobalt drier	2.0
PE wax paste	7.0
Gelling agent	0.5

*A maleic modified rosin ester (Hercules ink).
**A linseed isophthalic long alkyd resin.
***Aliphatic with 15 % aromatic.

Viscosity of ink after using these compounds was measured with rotator viscometer. Results shown in Table-3.

TABLE-3
RESULT OF APPLICATIONS OF ALUMATRANES

Sample	600	300	Plastic viscosity	Yield point
Without gelling agent	64	29	17	12
Commercial samples	164	112	52	60
A	161	112	49	53
B	160	109	51	58
C	149	99	50	49
D	125	84	41	43

The use of aluminum isopropoxide and other aluminum alkoxide in the manufacture of lithographic printing inks is well known. When they added to a mixture of resins during the manufacture of printing inks, alkoxides groups on aluminum react with carboxyl and hydroxyl groups present on the resins in the mixture to form both covalent and coordination bonds. Resins that used in lithographic ink, include alkyd resin, modified hydrocarbon resins, phenolic resins or mixture of them. According to these results, synthesized alumatrane show good rheological control in lithographic ink and their quality were compared respect to commercial alkoxide based samples. As a result of the reaction between the alumatrane and resins, viscosity increased. Increasing of viscosity can be monitored by plastic viscosity and yield point measurments.Yield point is a important factor for controlling of ink rheology.

Specific surface area for selected hydrolyzed samples given in Table-4. Surface area for the alumina obtained from alumatrane A and B, are significantly higher than the alumina obtained from alumatranes C and D. Interestingly, modification with triethanolamine has significant impact on the gel texture and specific surface area. Probably these result show that aluminum alkoxide has better interaction with TEA.

TABLE-4
SPECIFIC SURFACE AREA OF SELECTED SAMPLES

Alumatranes	SSA (m^2/g)
A	385
B	354
C	267
D	215

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