

Selected AbstractsVI. TonalonOppau, June 30, 1943Item #236Tonalon Manufacture 1939-1942

Many polyvalent metal salts are highly hydrolyzed in aqueous solutions. The metal hydroxide is the more important, and the acid, the less important component, as is the case with Al-formate and Al-acetate.

Tonalon is a basic Al chloride, $Al_2(OH)_5Cl$, which is produced, simultaneously with ethylenechlorhydrin, when ethyleneoxide is reacted with an aqueous solution of $AlCl_3$. It has the same acidity as Al formate or Al acetate but has an advantage of a higher content of effective Al_2O_3 . Only one sixth of the free hydroxyls in $Al_2(OH)_6$ is saturated with HCl.

Development started in 1931. German Patents issued - DRP 582,682 and 630,525.

Pilot plant operation: since 1933 to 1939, then commercial production.

First application in 1934: in Ramasit-Japan and in Curtaform in place of Al acetate.

Advantages of manufacture: simultaneous production of Tonalon and ethylenechlorhydrin which otherwise would have been made from the same ethylene oxide, but by reaction with HCl.

Method of manufacture: Al hydroxide is dissolved in HCl, under stirring and with introduction of live steam, to produce a solution of basic Al chloride. The liquid is saturated with ethylene oxide. The ethylene chlorhydrin is topped off in vacuo as a 40% solution. The residue is a Tonalon solution ready for use in Ramasit. Vacuum drying produces 100% Tonalon containing 46-48% Al_2O_3 .

Oppau, April 2, 1940Item #237Tonalon Production Report for 1939

The production of Tonalon during 1939 was 121,542 kg. The production (calculated as 100% product) of various grades was as follows:

(a) in the form of a 37% solution (Tonalon solution)	90,175 kg
(b) in the form of ground solid product for the dye industry (Solidogen AS)	11,201 kg
(c) in the form of reground solid product (Curtaform, Aluminagel) for the pharmaceutical trade or in the form of a special highly basic thick solution	2,800 kg 25 kg
(d) in the form of a ground solid product (Tonalon) with 46-48% Al_2O_3 content or in the form of an intimate mixture of Tonalon (80%) with Urea (20%) for the impregnation of cloth and other materials. This last mixed product was introduced to the trade in August 1939 as Tonalon H.	12,156 kg 6,060 kg

Zirconium Oxide Gel: The total production of zirconium oxide gel (calculated on the basis of 100% material) amounted to 9.305 kg. It was distributed (based on 100% material) as follows:

(a) in the form of a 45-48% solution (zirconium solution)	4,567 kg
(b) in the form of a ground solid product (zirconium oxide gel) with about 62% ZrO_2 for impregnation of cloth.	1,817 kg
By-product: Ethylene chlorhydrin	103,130 kg

Advertising Pamphlet on Tonalon

Item #239

Preparation of Tonalon H-Solution

Tonalon H can be dissolved in cold or warm tap water (drinking or river-water). The water should be free as possible from iron and coarse impurities.

To lessen the possibility of lump formation, Tonalon H powder is always added to the water and not conversely, the water to the powder. Tonalon H can be dissolved in a clean vessel, for example in a wooden vat, earthen- or enameled vessel. Metal vessels are to be avoided. The tap water solution can be prepared fresh and of any strength desired. However, Tonalon H solutions have good stability and it is recommended that stock solutions be prepared containing about 300 to 400 grams of Tonalon H per liter or kilogram.

The concentration of Tonalon H solution can be increased to 500 grams per liter; the stock solution recommended is a 37% by weight solution, which at 20°C has a specific gravity of 1.18 or 22° Beume. Acceleration of solution of the Tonalon H can be done by placing it in a basket hung in water, so that the concentrated solution will sink; stirring with air or by mechanical means is also helpful.

Tonalon H - Impregnation of Fabrics by a Single Bath Procedure

For less exacting requirements as to water repellency, a single impregnation in aqueous solutions of Tonalon H is sufficient. This can be accomplished with a 0.3-0.5% Tonalon H solution (3 to 5 g Tonalon per liter) with wool, cotton, linen and mixed fibers. By increasing the Tonalon H content, the impregnation effect cannot be increased. The cloth can be introduced into the bath in a dry or wet condition; the impregnation of dry cloth is somewhat more advantageous since it takes up the solution faster. Continuous operation is the fastest for large-scale work; washing machines, spool tubs, and jiggers can also be used for the impregnation procedure.

Tonalon H is recommended for mixing with Ramasit or wax emulsions whenever aluminum salts are to be used.

Tonalon H - Impregnation by a Two Bath Procedure

For a very durable water proofing, the cloth is conducted in the usual way into a soap bath (Bath I) and then into the Tonalon H Bath (Bath II). Depending upon the degree of water repellency desired, the fore- and after-treatment with more or less concentrated soap- and Tonalon H- solutions is carried out. Cloth, as for awnings and tents, should have the meshes sealed as much as possible. A 25 g per liter soap solution and a 20 g per liter Tonalon H solution are recommended. Heavy duck for paulins may require still higher concentrations.

Excellent water repellency may be imparted to garment fabrics and finished garments by using considerably lower concentrations. The treatment is applicable to artificial silk.

Drying Cloth Impregnated with Tonalon H from one- and two-bath Procedures

After impregnation, the cloth is squeezed out or centrifuged. The drying is carried out in the usual way on steam rolls, in a drying chamber, or on a tenter frame.

Tonalon H - Impregnation in Connection with Preventol-Preservation of Fabrics

Canvas, paulins, awnings and other technical textiles which remain in moist condition for long periods of time or come in contact with soil, rapidly deteriorate from mold and fungi. Liquid Preventol-N is recommended as a fungicidal agent. It should be added to the soap solution in the process of waterproofing with Tonalon H.

One or more pages are missing in this item. Item #240

The page available refers to ethylene chlorohydrin obtained, perhaps in Tonalon production; a table gives the raw materials used for the product, evidently Tonalon, and the zirconium analog. The salting out of ethylene chlorohydrin from the 40-volume percent solution with soda is mentioned. Since one or more pages are missing, it is difficult to summarize the item.

Part of Flow Sheet on Tonalon Manufacture. Item #241

Oppau, April 30, 1940 Item #242

About the Absorption of Ethylene Oxide by Aluminum Chloride Solutions

By the reaction of ethylene oxide with an aluminum chloride solution, ethylene chlorohydrin and aluminum hydroxide are obtained. However, if one introduces ethylene oxide in such an amount, that a small amount of chlorine remains as shown in the formula, $Al_2(OH)_5Cl$, one obtains after removal of the chlorohydrin, a solution designated as "Tonalon", which is best employed as an impregnating material for textiles, as a starting material for the preparation of "Ramasit" and for other different purposes.

The paper deals with the absorption of ethylene oxide in aluminum chloride solution, containing 143 g/l Al_2O_3 and 196 g/l

chlorine, at room temperature and at 60°C, with a gas stream of 50 liters of CO₂ and 2.5 liters ethylene oxide per hour; tables are given for reaction time and per cent ethylene oxide unabsorbed. Table III gives conditions for a one tower absorber through which gas streams of ethylene oxide, of varying percentages, were passed; new make-up solutions of aluminum chloride were used in the tower, or were continuously added to the tower. Data for a two absorber tower system is given in Table IV. A laboratory apparatus sketch is given in Figure I, and a flow sheet is given for the continuous preparation of Tonelon from dilute ethylene oxide gas streams in Figure II. It consists of a two-stage absorption of ethylene oxide at 60°C and 20°C from gases circulated countercurrently to the flow of AlCl₃ solution. The saturated solution is passed to the continuous vacuum still in which ethylene chlorohydrin is taken overhead and Tonelon solution is recovered as bottoms.

Oppau Laboratory Report, August 25, 1943

Item "243

"The Preparation of Aluminum Triformate from Aluminum Chloride Solutions with Particular Regard to the Utilization of Aluminum Chloride Spent Liquors"

The following items were considered:

A. Technical Application of Aluminum Formate

The availability of formic acid and its salts lead to the consideration of preparing aluminum formate since aluminum acetate was being used extensively in water-proofing preparations.

B. Known Methods for the Preparation of Aluminum Formate

Aluminum formate solutions have been prepared by the following methods:

- (1) Aluminum Sulfate + Calcium Formate
- (2) Aluminum Sulfate + Sodium Formate
- (3) Aluminum Sulfate + Barium Formate
- (4) Aluminum Hydroxide + Formic Acid

The above methods suffer from the difficulty of isolating the aluminum formate from the solutions (1,2,3) whereas method (4) requires large quantities of formic acid and approximately 50% of the formate remains in solution. A new procedure, free from these difficulties, was to be developed.

C. A New Procedure for the Preparation of Aluminum Triformate

(1) Crystallization in the Presence of a Foreign Salt

Table I shows the effect of using salts as sodium chloride, potassium sulfate, calcium chloride, etc., on yield improvement in crystallization of aluminum triformate from its solutions. The yield is better when sulfates and chlorides are used than when nitrates are used. Despite the fact that only a trace of chlorine is present in the aluminum triformate when a chloride is used to aid crystallization, chlorides in the presence of dyes cause a "selting-out" effect. As a result of this contamination, it was concluded that by the application of the "common-ion" effect principle, a purer aluminum triformate would be obtained; that is, an ion common to the soluble salt product would decrease the solubility of the salt. In the ensuing work formic acid was used for this purpose.

(2) Aluminum Triformate by Double Decomposition with Formation of a More Soluble Foreign Salt

(a) Double decomposition of aluminum chloride with sodium formate

Work was carried out on this method of double decomposition, using formic acid for the purpose mentioned above; a yield of 95% of the theoretical was obtained. When calcium formate was used a yield of only 60.5% of the theoretical was obtained; this is explained by stating that the exceedingly large quantity of calcium chloride formed interferes with the reaction of aluminum hydroxide; a small quantity of calcium chloride is not deleterious as shown in Table I and Table III.

(b) Double decomposition of aluminum chloride wastes with sodium formate and formic acid

The utilization of aluminum chloride wastes, obtainable from the Friedel-Crafts reactions and other reactions of large chemical industries has been a problem of long standing. These aluminum chloride wastes are more or less contaminated with iron chloride.

Aluminum chloride wastes from the lubricating oil plant at Leuna and from the paraffin wax oxidation plant at Oppau were tabulated as to their composition. In experiment one, with the

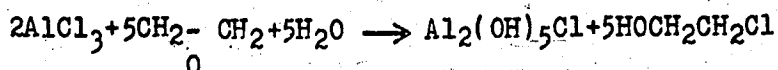
aluminum chloride waste from the oil plant at Leuna, the waste was treated with sodium formate and formic acid, after seeding the solution with 10 g of aluminum triformate, and working up the crystallized Al formate, a yield of 88% of the theoretical was obtained; its iron content was 0.15% FeO, thus proving that a pure product can be made from waste AlCl₃.

In experiment two, with the aluminum chloride waste from the paraffin wax oxidation plant at Oppau, by a similar treatment as mentioned above, 83% of the theoretical amount of pure Al formate was obtained. The iron content was only 0.15% FeO.

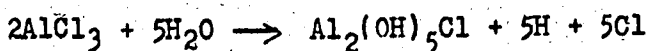
(c) Double decomposition of highly basic aluminum chloride solutions with formic acid in the presence of sodium or calcium formate

Various methods of preparing highly basic aluminum chloride solutions are shown by the following equations:

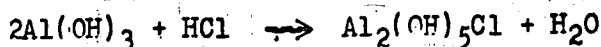
(1) In the Tonalon Process:



(2) Electrolysis Method:



(3) Peptization of Aluminum Hydroxide with Acid:



Laboratory data is tabulated showing the yields of aluminum triformate from highly basic aluminum chloride solutions (Tonalon solutions) in reaction with sodium or calcium formate and formic acids. A brief summary of the yields is given as follows:

	<u>Sodium</u> <u>Formate</u>	<u>Calcium</u> <u>Formate</u>
	% Yield (of theo.)	
Al(OH) ₅ Cl (pure)	85	
"	92.1	
"		90
"	95	
Al(OH) ₅ Cl (from spent liquor)	90.5	
"		91
"		90
Al(OH) ₅ Cl (from nitrate) (pure)	87	

The aluminum triformate obtained by this method is very pure and completely soluble in hot water; the sodium chloride content varies from 0.2 to 0.5%, while the iron content as FeO is not higher than 0.2%.