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PROCESS FOR REDUCING THE REFRACTORY HALIDE CONTENT OF AN ALKYL AROMATIC EMPLOYING AS CONTACT MATERIAL AN ALKALINE EARTH METAL COMPOUND CONSISTING OF THE OXIDES AND CARBONATES OF CALCIUM

Robert W. Rosenthal, Pittsburgh, and William L. Walsh and John G. McNulty, Glenshaw, Pa., assignors to Gulf Research & Development Company, Pittsburgh, Pa., a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

The refractory chloride content of an alkyl aromatic compound can be reduced by treating said compound with an alkaline earth metal compound, such as calcium oxide, at elevated temperatures. The process is useful to prepare detergent alkylates having reduced chloride content and therefore superior properties.

BACKGROUND OF THE INVENTION

Chlorine is frequently an undesirable impurity in certain materials. For example, the presence of chlorine in the so-called detergent alkylates is undesirable because of its irritating effect on the skin. One would expect that such undesirable chlorine compounds could be removed by ordinary and well-known techniques for the removal of such impurities, for example, by caustic scrubbing. Unfortunately this is not true in many instances. It has been found, in fact, that the chlorine is frequently chemically bound to compounds whose freedom from such chlorine is important for successful commercial application of said compounds. By the practice of the process described and claimed below it is possible to eliminate these and other problems by reducing the chlorine content of chloride-containing compounds.

Aromatic compounds such as benzene, xylene, naphthalene, anthracene, etc., can be alkylated with a mixture of primary and secondary normal alkyl monochlorides, wherein the alkyl portion thereof has, for example, from 10 to 16 carbon atoms, to produce an alkyl aromatic mixture. This mixture is commonly referred to as "detergent alkylate," since it can be subsequently sulfonated in known manner to produce a detergent. The desired alkylation is typically carried out in the presence of about 3 to about 10 weight percent of a Lewis acid, such as aluminum chloride, in which the reaction system can contain from about 5 to about 15 moles of aromatic per mole of alkyl halide. Normal alkylation conditions include temperatures ranging from about 15° to about 70° C., pressures ranging from about 250 mm. Hg to about 100 p.s.i.g. and reaction periods of about ½ to about 1½ hours. Upon completion of the reaction the catalyst is usually removed as a sludge and the mixture washed free of hydrogen chloride. The mixture can then be fractionated at atmospheric pressure and temperatures ranging from about 70° to 85° C. to remove any unreacted aromatic compounds therefrom. Thereafter, it is customary to vacuum distill the mixture, at pressures of from about 1 to about 20 mm. Hg and temperatures ranging from about 100° to about 200° C. to recover, sequentially, unreacted paraffin and the desired alkyl aromatic compounds or mixtures thereof, termed "detergent alkylate." This detergent alkylate frequently contains chlorine which is often undesirable from the point of view of the end use of the product. These detergent alkylates can contain from about 100 to about 5000, but in general contain from about 100 to about 500, parts

per million of chlorine. Those detergents which are to be used in the home for such general purposes as dishwashing, general cleaning etc., desirably should not be irritating to the skin. Chlorine containing detergents, which are irritating because of their chlorine content, are consequently less desirable for general purpose household use than chloride-free detergents and in fact soap and detergent manufacturers frequently specify the maximum tolerable chloride content, which detergents or detergent alkylates purchased by them can have, as less than 50 p.p.m. It is thus particularly desirable, prior to sulfonation, to have the detergent alkylate as free of chlorine as possible.

It is believed that the undesirable chlorine components referred to above are not merely mixed in with the detergent alkylate but may be firmly attached to some part of a molecule by chemical bonding. This assumption is supported by the fact that such techniques as caustic scrubbing and distillation results in a product that still contains a significant quantity of chlorine. Such chlorine is termed herein "refractory," indicating that it is heat resistant, that it cannot be removed by distillation.

SUMMARY OF THE INVENTION

We have found that the refractory chlorine content of an alkyl aromatic compound can be reduced by treating said compound with an effective amount of an alkaline earth metal compound selected from the group consisting of the oxides and carbonates of calcium. Calcium oxide is preferred.

As indicated above this process has particular utility in removing refractory chloride from a detergent alkylate.

The process is quite simply accomplished by merely contacting the material which contains refractory chloride with one or more of the defined alkaline earth metal compounds at a temperature of from about 150° to about 500° C., preferably from about 200 to about 400° C., at pressures which can range from about atmospheric to as high as about 500 p.s.i.g. The process is preferably conducted at atmospheric pressure. The amount of alkaline earth metal compound employed can vary over wide ranges and only such amount thereof need be used that will be sufficient to obtain the desired contact with the material containing the refractory chloride. In general, the amount of alkaline earth metal compound that need be present relative to the material containing the refractory chloride, on a weight basis, can be from about 10:1 to about 1:10, preferably from about 5:1 to about 1:5. The amount of contact required between the two can also vary, for example at least about 1 second and preferably from about 5 to about 10 seconds. The process can be conducted in a wide variety of equipment in either continuous or batchwise operation. One advantageous aspect of our invention is that the process can be run continuously and in a preferred embodiment a hollow tube packed with calcium oxide and heated to the desired temperature is used. It should be noted at this point that not all methods of treatment of materials containing refractory chloride are equivalent, even when the same alkaline earth metal compounds are used. Thus, for example, when a detergent alkylate containing chlorine was distilled over calcium oxide, the results obtained were not nearly as good with respect to halide reduction as were those obtained when the material was treated in accordance with the instant process. These results can be seen in Example II.

As will be seen from the following examples, treatment of materials containing refractory chloride results in a significant decrease in chlorine content. The precise range of chlorine content of the product material cannot be stated with greater particularity because the actual reduction in chlorine content can be controlled at will by

varying such factors as contact time, amount of alkaline earth metal compound etc.

The process of this invention can further be understood by reference to the following:

DESCRIPTION OF THE PREFERRED EMBODIMENTS

These two examples show that the chloride content is not significantly reduced by treating chlorine containing materials in the usual manner. The examples also lend weight to the theory that the chlorine is in some way bound to the material reduction of whose chlorine content is desired.

EXAMPLE I

This example illustrates the utility of the process of the instant invention in reducing the chlorine content of a detergent alkylate.

A detergent alkylate was prepared as follows: Five gallons (14.5 kilograms) of C_{10}–C_{14} normal paraffins (4.6% C_{10}; 18.2% C_{11}; 22.2% C_{12}; 34.3% C_{13}; 20.7% C_{14}) were chlorinated at 50–65° C. in the presence of 150 watt lamps until 1.8 kilograms of chlorine added. The product was purged with N_2 to remove excess HCl. The product was then added, over a period of 28 minutes, at a temperature of 21–22° C. to a mixture of 21.5 kg. of benzene and 0.4 kg. of $AlCl_3$. The mixture was stirred for one hour longer and then the catalyst layer was drawn off. The solution was washed three times with two-gallon aliquots of water, once with one gallon of 5 percent NaOH and twice with two-gallon aliquots of water. The product detergent alkylate was analyzed and found to contain 103 p.p.m. of chlorine.

Fifty grams of the detergent alkylate prepared above were dripped through a column, 63.5 cm. x 1.25 cm. I.D., of CaO, heated at 400–410° C. over a two hour period. Analysis of the effluent showed the chloride concentration to have dropped to less than 0.5 p.p.m.

EXAMPLE II

This example illustrates the proposition that not all methods of contacting chlorine containing compounds with the alkaline earth metal compounds useful in the instant invention are capable of giving equivalent results.

Fifty grams of the detergent alkylate prepared in Example I above, containing 103 p.p.m. of chlorine were distilled from 10 g. solid CaO through a 12 inch Vigreux column. The product distilled at 110–120° C. at 1 mm. Hg pressure and was found to contain 84 p.p.m. chlorine.

It is thus seen that distilling the chlorine containing material over CaO is not nearly as effective in reducing the chlorine content as is treatment of the same material by the process of the instant invention.

Obviously many modifications and variations of the invention as hereinabove set forth, can be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for the reduction in the refractory chloride content of an alkyl aromatic detergent alkylate which comprises contacting the same solely with an alkaline earth metal compound selected from the group consisting of the oxides and carbonates of calcium at a temperature of about 200° to about 500° C.

2. The process of claim **1** wherein said alkaline earth metal compound is calcium carbonate.

3. The process of claim **1** wherein said alkaline earth metal compound is calcium oxide.

4. The process of claim **1** wherein said alkyl aromatic detergent alkylate is an alkyl benzene wherein said alkyl has from 10 to 16 carbon atoms.

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PAUL M. COUGHLAN, JR., Primary Examiner

J. M. NELSON, Assistant Examiner

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