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PROCESS FOR ESTERIFYING POLYMERIZED
OLEFINS

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This invention relates to improved detergent aids and method of preparing the same. It particularly relates to detergent aids prepared from olefin polymers, and especially to those olefin polymers having from 10 to 30 carbon atoms in the molecule secured by polymerizing olefins having from 3 to 6 carbon atoms in the molecule. By the term "detergent aids" it is meant to include wetting, dispersing and emulsifying agents and detergents.

Many different types of wetting agents and detergents are already known and the present detergents are to be distinguished from detergents prepared from relatively straight chain olefins such as those secured from cracked wax or from dehydrogenated saturated paraffins. Although the exact structure of the olefin polymer compounds having from 10 to 30 carbon atoms and secured by the polymerization of low molecular weight olefins is not exactly known, it is reasonably certain that these compounds contain a number of carbon side chains. This feature makes the detergent aids derived from such compounds particularly desirable in that they have a lower melting point, they are more oil and less water soluble, and their germicidal value is considerably higher than that of detergent aids produced from substantially straight chain olefins.

These detergent aids are prepared by treating a low molecular weight polymerized olefin such as isobutylene dimer, trimer and tetramer, amylene dimers and trimers and the dimers and trimers of hexylene with a strong mineral polybasic acid such as sulphuric acid, and then neutralizing with an alkali as, for example, sodium hydroxide. These highly branched olefin polymers, preferably those having from 12 to 20 carbon atoms in the molecule and still containing one double bond per molecule, are treated preferably with sulphuric acid under conditions to form a satisfactory olefin polymer sulphuric acid reaction product, and then neutralized with an alkali such as sodium hydroxide, potassium carbonate, onium bases, etc. in order to produce the desired detergent.

The olefin polymers may be prepared from olefins which are substantially in the pure state, or they may be prepared by treating hydrocarbon fractions containing olefins, as for example, those hydrocarbon fractions from petroleum refinery distillation, cracking and naphtha reforming operations. Materials such as propylene, ethylene, acetylene, butadiene, isoprene or extracted olefins or polymers from vapor phase

cracked gasoline and the like, may be polymerized to produce polymers having from 5 to 30 carbon atoms in the molecule. Gaseous olefins such as ethylene, propylene, butylenes and amylenes and mixtures of these, which are present in refinery gases from cracking, distilling and naphtha reforming operations may also be polymerized to secure satisfactory polymers. The preferred raw materials are ethylene, propylene, butylene, amylene and hexylene. The term "polymers" is intended to also include co-polymers of these compounds, i. e., a polymer of two dissimilar monomers, such as a polymer of isobutylene and normal butylene.

These olefins may be polymerized in any manner which will give the desired polymer. One method is to polymerize olefins by means of catalysts such as boron fluoride, aluminum chloride or other volatile metallic halides above about 32° F. or by treating with dilute or strong sulphuric acid or liquid phosphoric acid. Olefins may also be polymerized by heating under suitable pressure and temperature conditions, at about 500–900° F. for example, and 200–3000 pounds per square inch or more. Catalytic masses such as clay, alumina, charcoal, sodium metaphosphate, anhydrous ferric chloride, bauxite and silica gel, may be employed, as well as catalysts of the types of charcoal impregnated with phosphoric acid. Liquid catalysts such as sulphuric acid and phosphoric acid or the sulfates or chlorides of various metals may be employed. The conditions of the polymerization reaction may be widely varied in order to secure a satisfactory polymer product. For instance, in the case of iso-olefin polymerization, dilute acids at elevated temperatures are employed. For example, with isobutylene polymerization is carried out with 65% sulphuric acid at 100–200° F., say 165° F.

The polymers are then treated with strong polybasic mineral acid as, for example, strong or fuming sulphuric acid, chlorosulphonic acid, phosphoric acid, and the like. The treating agent is preferably strong sulphuric acid of approximately 90% concentration or fuming sulphuric acid containing as high as 20% oleum. The reaction is preferably carried out at a temperature from 10° to –20° C. although if the time of contact is reduced, somewhat higher temperatures may be employed. The reacted olefin reaction product is neutralized with alkali to produce neutralized olefin polymer acid reaction product having desirable wetting and detergent properties.

The following examples serve to illustrate meth-

ods of preparing the detergent aids of the present invention:

Example 1

100 parts by weight of a cracked petroleum butane type fraction containing 10.6% isobutylene was treated in a tower with 55 parts of 70% sulphuric acid at 28 to 32° F. and atmospheric pressure. The acid extract containing 9 parts isobutylene was then separated and heated in a packed copper tube having an exit temperature of 248° F. About 7 parts of polymer were separated from the acid, the polymer containing 12% dimer and 88% trimer of isobutylene. These products were then separated by distillation.

To 100 parts of the tri-isobutylene was added slowly 61 parts of sulphuric acid containing 20% sulphur tri-oxide. The mixture was vigorously stirred and the reaction temperature kept below 120° F. during the addition of the fuming sulphuric acid. After the acid was entirely added, the temperature was increased to about 140 to 160° F. and maintained at this temperature for about 1½ hours, during which it was vigorously stirred for the first three-quarters of an hour. The material was then neutralized by adding 133 parts of 30% sodium hydroxide solution. To this solution was then added 123 parts of 91% isopropyl alcohol and the entire mixture heated under reflux conditions for two hours. The mixture was then allowed to stand at room temperatures for approximately 48 hours, during which it separated into three distinct layers. The upper layer was unreacted material while the middle layer was a neutralized olefin polymer sulphuric acid reaction product consisting mainly of the sulfate and having detergent and wetting properties and a lower water layer. The respective layers were separated by decantation and the middle layer evaporated in an oven resulting in a yield of 41.3 parts of a dark viscous liquid having detergent and wetting properties.

The wetting numbers of the detergent were as follows:

	Wetting number seconds *
0.2% solution of the detergent in distilled water	193
0.2% solution in hard water, (Ca++—300 parts/million)	126

*Wetting number is measured by the disc method and represents the number of seconds it takes for a small circular disc (2 cm. diam.) of cotton canvas to become completely wetted when gently laid on the surface of an 0.2% solution of the soap in water.

Example 2

A charge of cracked petroleum butane type fraction was agitated at 35–40° F. under 3 pounds gauge pressure. Boron fluoride gas was led into the mass at a rate equal to 40 in. of water pressure drop through a ¾ in. orifice. When the reaction had started, the feed was added at a rate of 250 gals./hr. until the agitator overflowed into a still, then the rate was cut to 100 gals./hr. During the reaction the temperature increased to 100° F. and the pressure went up to 7–8 pounds gauge. The polymer obtained was fractionated by distillation and the tri-isobutylene separated.

To 100 parts of tri-isobutylene was added 60.7 parts of 96% sulphuric acid. The acid was added slowly and the reaction temperature was maintained below 120° F. and vigorous stirring employed during the addition of the sulphuric acid. After the sulphuric acid was added, the reaction mixture was heated to a temperature between

140° and 160° F. for 1½ hours in which vigorous stirring was employed for the first three-quarters of an hour. To this mixture was then added gradually 133 parts of 30% sodium hydroxide solution. To the neutralized solution was then added 123 parts of 91% isopropyl alcohol and the entire mixture was heated under reflux conditions for 2 hours. The product was then allowed to stand and a three-layer separation occurred. The neutralized isobutylene polymer sulphuric acid reaction product middle layer was separated by means of decantation. The upper layer was re-extracted with 91% isopropyl alcohol and the extracts were combined with the separated middle detergent layer which was then evaporated to dryness in a steam bath. A yield of 8.8 parts of semi-solid pasty material of a light brown color resulted, which as seen from the following data, possesses excellent wetting characteristics in dilute acid and in hard water:

	Wetting number seconds
0.2% solution in distilled water	39
0.2% solution in hard water (Ca++—300 parts/million)	65
0.2% solution in acid water (3% sulphuric acid)	33

*Wetting number is measured by the disc method and represents the number of seconds it takes for a small circular disc (2 cm. diam.) of cotton canvas to become completely wetted when gently laid on the surface of an 0.2% solution of the soap in water. Pure water generally has a wetting number of between 70,000 to 100,000.

Other suitable polymer materials which can be converted to excellent detergent aids are:

Polymers of gaseous olefins obtained by treating the latter with phosphoric acid at 200–250° F. and 400–500 pounds pressure.

Polymers of propylene obtained by treating the olefin with alumina-silica catalysts or activated or raw clays.

Polymers of lower olefins obtained by polymerization with acid treated bentonites.

Polymers obtained by depolymerization of higher hydrocarbon polymers.

The above invention is not to be limited by any theory or method of operation but only by the following claims in which it is desired to claim all novelty in so far as the prior art permits.

We claim:

1. Process for preparing detergent aids comprising polymerizing an olefin then separating a polymer fraction having from 10 to 30 carbon atoms in the molecule and treating the olefin polymer fraction with a strong polybasic mineral acid, and neutralizing the olefin polymer acid reaction product to secure a product having detergent and wetting properties.

2. Process for preparing detergent aids comprising polymerizing olefins having from 3 to 6 carbon atoms in the molecule separating therefrom polymer fractions having from 12 to 20 carbon atoms in the molecule then treating said polymer fractions with a strong polybasic mineral acid followed by neutralization of the olefin polymer acid reaction product with an alkali to produce a reaction product having detergent and wetting properties.

3. Process in accordance with claim 2 in which said strong polybasic mineral acid is sulphuric acid and said alkali is sodium hydroxide.

4. Process in accordance with claim 2 in which said strong polybasic mineral acid is fuming sulphuric acid and said alkali is sodium hydroxide.

5. Process comprising polymerizing a butane

cracked petroleum fraction to give a product predominating in trimer, separating the trimer by distillation, sulfating said trimer, and neutralizing the product to produce a detergent aid.

5 6. The process comprising the steps of separating from a cracked petroleum product an olefin compound, treating the olefin compound with a polymerizing agent, separating the polymerized product into a fraction containing substantially
10 pure trimer, treating the trimer with concentrated sulphuric acid to produce a sulphonate, and neutralizing the sulphonate to produce the sodium salt of a polymerized iso-olefin sulphonic acid as a detergent.

15 7. The process comprising the steps of polymerizing a cracked petroleum product, separating the polymerized product into a fraction contain-

ing substantially pure trimer, treating the trimer with concentrated sulphuric acid at a low temperature to produce a sulphonate, and neutralizing the sulphonate to produce the sodium salt of a polymerized iso-olefin sulphonic acid as a detergent. 5

8. The process comprising the steps of polymerizing isobutylene, separating the polymerized product into a fraction containing substantially pure trimer, treating the trimer with concentrated sulphuric acid at a low temperature to
10 produce a sulphonate and neutralizing the sulphonate to produce the sodium salt of a polymerized iso-olefin sulphonic acid as a detergent.

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