The present invention relates to washing, wetting and emulsifying agents which are salts of acids resulting from the reaction of maleic anhydride and similar aliphatic carboxylic acids or anhydrides containing the alpha-beta-enal grouping:

\[ R = R - \text{enal} \]

with olefins, alkyl halides and alcohols. This application is a continuation-in-part of my prior application, Serial No. 181,597, filed December 24, 1937, which has issued as Patent No. 2,283,214, and relates specifically to the process of making such agents by the reactions of alkyl halides, particularly tertiary alkyl chlorides, with maleic anhydride and similar aliphatic carboxylic acids or anhydrides containing the alpha-beta-enal grouping.

Heretofore it has been known that olefins condense with maleic anhydride to produce alkene-succinic acids or anhydrides, which reaction may be generally represented as:

\[
\begin{align*}
R = R - &\text{enal} \\
\rightarrow &R - HC - CO \\
\rightarrow &H - CO
\end{align*}
\]

In my copending application, Serial No. 181,597, referred to hereinafter, I have shown that alkyl halides condense in the same manner with maleic anhydride and similar carboxylic acids to produce alkene-succinic acids or anhydrides, according to the following reaction:

\[
\begin{align*}
R = R - CH - &\text{enal} \\
\rightarrow &R - HC - CO \\
\rightarrow &H - CO
\end{align*}
\]

It is to be noted that the radical of the alkyl chloride, which was a saturated radical, appears in the final compound as an unsaturated radical.

As a result of this discovery, acids of this type may be readily prepared without conversion of alkyl halides to olefins, which was heretofore considered essential, and it is furthermore possible to provide these acids and their salts from alkyl halides which, in many cases, are more readily obtainable than the corresponding olefins.

The invention is adaptable in general to the production of alkenoacids having the general structure:

\[
R - \text{enal} - COOH
\]

in which R is selected from the group consisting of hydrogen, alkyl and carboxyl radicals. These acids correspond in general to the condensation products of olefins or alkyl halides with carboxylic acids or acid anhydrides having an alpha-beta-enal grouping.

My process is generally adapted to the condensation of maleic anhydride and similar unsaturated carboxylic acids containing the alpha-beta-enal grouping, examples of which are fumaric and maleic acid, HOOC-CH=CH-COOH, itaconic acid, CH=CH(COOH)CH=CH-COOH, citraconic acid, CH(=C(COOH))CH=CH-COOH, acrylic acid, CH=CH-COOH, and crotonic acid:

\[
\text{CH}_2\text{CH} = \text{CH} - \text{COOH}
\]

The formulae of these acids can be represented generally as:

\[
R - C - \text{enal} - COOH
\]

in which R has the foregoing significance. Because of their ease of condensation, and since they are readily obtainable, the anhydrides of dicarboxylic acids of this series are preferred as the starting materials for condensation reaction to produce the compounds contemplated in the invention. Maleic anhydride is the most common and most readily available acid anhydride of this series and hence is particularly considered throughout this specification. Aromatic acids such as phthalic acid, in which the reactive portion of the alpha-beta-enal grouping is partly incorporated in the phenyl nucleus, are not operative.

Alkyl halides, which may be used in the process of the present invention, include alkyl chlorides, bromides and other halides. The invention is directed particularly to the use of tertiary alkyl halides, which are much more reactive than secondary or primary halides. For the production of alkeno-succinic and other alkeno-substituted acids of the series, which are to be used for the preparation of water-soluble salts useful as washing, wetting and emulsifying agents as described in my prior copending application, alkyl halides having an alkyl group which contains from five to sixteen carbon atoms, inclusive, are contemplated. Chlorides are the preferred halides and, for this purpose, amyl chlorides, hexyl chlorides, heptyl chlorides, octyl chlorides, nonyl chlorides, decyl chlorides, undecyl chlorides, dodecyl chlorides, tridecyl chlorides, tetradecyl chlorides, hexadecyl chlorides and the like, particularly tertiary chlorides of this designation, are exemplary.

In conducting the process of the invention, the unsaturated acid containing the alpha-beta-enal grouping is heated with the alkyl halide.
while the mass is stirred. The reaction is generally conducted at reflux temperature and the hydrogen chloride which is evolved is allowed to escape or is collected. The reaction period at reflux temperatures which is required to effect the condensation to produce a good yield is somewhat long in some cases and for this purpose the use of catalysts is desirable, especially in the case of alkyl chlorides of low boiling point. The refluxing temperatures when such low-boiling chlorides and reactions are not used is not high enough to provide an effective reaction and the periods which are required to obtain any substantial yield of alkene-succinic acid are extremely long. The use of catalysts to shorten the reaction periods when higher-boiling alkyl chlorides are used is also advantageous. In reacting chlorinated kerosene fractions, temperatures of about 150°C to 200°C may be easily maintained by gentle reflux, but the addition of catalyst shortens the reaction period substantially.

As catalysts for the reaction, acidic metal chlorides or other halides may in general be used. Zinc chloride is especially effective, but antimony chloride, stannic chloride, aluminum chloride, and ferric chloride may be used with advantage. Only a small proportion, about 1% or less than 5% of zinc chloride, for example, is required for catalytic effect.

The proportion of the reacting substances may be varied widely. Theoretically equimolecular quantities of alkyl halide and the acid are required. Generally when equimolecular quantities are used the reaction does not proceed to completion, and to facilitate it, it is preferable to add an excess of one reactant, preferably the alkyl halide, since it is easily recoverable from the reaction mass and the recovery and purification of the resulting alkene-acid is facilitated.

The reaction may be conducted in the presence of an inert solvent. For example, when using chlorinated kerosene fractions as the alkyl halide reactant, I prefer to use "underchlorinated" fractions, that is, kerosene fractions which have not been chlorinated to the full extent required to produce alkyl monochlorides, since in chlorinating such fractions, the proportion of dichlorides and other polychlorides which are produced increases as the extent of the chlorination increases. In reacting low-boiling alkyl halides, a higher-boiling inert solvent for these materials, such as kerosene fractions, may be used to permit higher refluxing temperatures.

The recovery of the alkene acids from the reaction mixture may be effected by any of the conventional methods. After reacting maleic anhydride with tertiary-dodecyl chloride or a chlorinated kerosene fraction, for example, an aqueous solution of sodium hydroxide may be added to the reaction mass, whereupon the excess alkyl halide will separate as a supernatant layer. The acid that has formed dissolves in the aqueous layer in the form of the respective sodium salt. The aqueous layer after separation is then acidified to precipitate the alkene-succinic acid which was formed, while the unreacted maleic acid remains in solution. Before separating the precipitated acid mass from the aqueous solution it is advantageous to add a water-immiscible solvent such as chloroform to the mixture to reduce the viscosity and take up the dodecane-succinic acid remaining dissolved in the maleic acid aqueous layer. The two layers are then separated, the acid product is recovered from the chloroform layer, and the products in the aqueous layer also are recovered. Obviously, other methods, some of which are disclosed in Examples I and III, which follow, may be used for the separation.

The separation may be dispensed with after merely removing unreacted alkyl halide, for example, by distillation in vacuum or with steam, as described in Example II, inasmuch as small amounts of unreacted maleic or other acid which may be present generally have no detrimental effect in the particular contemplated use.

The alkene-substituted acids of the invention are of value in the preparation of detergents, polishes, waxes and hydrocarbon oil emulsions, insecticidal emulsions, cold-water paints and as thickening agents for rubber latex, as flotation reagents, as pigment-treating agents to improve dispersibility and grinding properties, as rubber compounding ingredients and the like. They are of special value for the preparation of detergents for use in hard water, for which purpose they are equal to or superior to sulfonated detergents such as alkylbenzenesulfonic acids. The calcium salts of the compounds are soluble in water, and the compounds are well-adapted for use in alkaline washing operations.

The following examples are illustrative of the methods of practicing the invention:

**Example I.—Decene-succinic acid**

One-fifth mol (35.3 grams) of tertiary-decyl chloride obtained by chlorinating a commercial petroleum fraction was heated under reflux with one-fifth mol (20 grams) of maleic anhydride. Evolution of hydrogen chloride started at 170°C. Refluxing started at 178°C. The vapor temperature did not gradually rise as observed when condensing olefins with maleic anhydride. Heating was discontinued at the end of 50 hours, at which time evolution of hydrogen chloride had practically ceased. The reaction product was made alkaline with 5% sodium hydroxide solution and the light, oily fraction of decyl chloride was separated. The sodium salt solution was made acid to Congo red with 10% hydrochloric acid solution and the precipitated acid was separated from the aqueous solution. The acid and water layers were thoroughly extracted with chloroform. Evaporation of the chloroform extracts yielded a dark, gummy mass. This product assayed 85% decene-succinic acid. The sodium salt of the decene-succinic acid was prepared by adding sodium hydroxide solution in quantity just sufficient to neutralize the acid, according to the titration results. By dilution with water, solutions of the sodium salt of desired concentration may be prepared for use or the sodium salt may be recovered by evaporation or other suitable methods.

**Example II.—Undecene-succinic acid**

A kerosene fraction having an Engler boiling range as follows:

Initial drop—190.5°C.
50% at 203°C.
End at 227.5°C.

was used as the source of alkyl chlorides. This fraction corresponds approximately to a mixture of undecanes and dodecanes, with perhaps a small proportion of tridecane and tetradecanes. It was then chlorinated to 60 mol per cent, that is, to an extent corresponding to 60% of that amount required stoichiometrically to convert the alkanes to alkyl monochlorides.
Into a flask provided with a reflux condenser and thermometer was charged 98 grams (1 mol) of maleic anhydride and 568 grams of the chlorinated kerosene fraction, which corresponds approximately to 1.8 mol of alkyl chlorides. The flask was heated until the charge reached 150° C, at which point distillation started. The molten maleic anhydride remained at the bottom but after heating for about 1 hour, after which time the temperature reached 165° C, the mixture was homogeneous. The mixture was heated at gentle reflux for a total of 45 hours.

To recover the product, the excess kerosene and chlorinated kerosene fraction were removed by distillation with steam. The alkene-succinic acids which remain can be purified and recovered as such. However, the residue was neutralized with sodium hydroxide solution and dried on a drum drier. A light brown powder, which consists principally of sodium salts of undecene-succinic acids and dodecene-succinic acids, was obtained.

Example III.—Dodecene-succinic acid

A kerosene fraction having a boiling range of 205° to 245° C, which corresponds to a dodecane to tridecane fraction, was chlorinated until chlorine was substituted to the extent of 46% of that required stoichiometrically to convert the kerosene (calculated as dodecane) to monochloride. The chlorinated kerosene was fractionated and the fraction having a boiling range between 107° and 130° C, at a pressure of 8 mm. of mercury was used.

Into a glass flask provided with a stirrer, thermometer, and a reflux condenser was placed 125 grams of maleic anhydride. The flask was heated in an oil bath until the temperature of the maleic anhydride reached 185° C. A small amount of the chlorinated kerosene fraction was then added but no reaction or evolution of hydrogen chloride was observed. A small quantity of anhydrous zinc chloride was then added, while the mixture was stirred, whereupon an immediate evolution of hydrogen chloride occurred. With the temperature of the bath at 190° C, the addition of the chlorinated kerosene was continued dropwise over the course of about 2 hours until a total of 258 grams was added. The reaction mixture was stirred continually and maintained at a temperature of about 180° to 185° C, for 18 hours.

The product was recovered and purified by treating the cold reaction mixture with about 100 cc. of water and sufficient benzene to dissolve the product. The two layers were separated and the benzene layer was filtered and washed about four times with small portions of water. The washings were added to the recovered aqueous layer. The desired product, which comprises the alkene-succinic acids and which is dissolved in the benzene layer, is then recovered by extracting the benzene layer repeatedly with sufficient quantities of dilute sodium hydroxide solution to remove the alkene-succinic acids. These aqueous extracts were then combined with the aqueous layer. This aqueous layer may be treated with steam, if desired, to remove steam-volatile impurities. The aqueous layer was then cooled and acidified with an excess of hydrochloric acid. The mass which separated out, and which was a mixture of dodecene-succinic and tridecene-succinic acids, was washed while warm with water. It may be converted to sodium salts by dissolving it in ethyl alcohol and neutralizing with sodium hydroxide.

For the preparation of the sodium salts, the ethyl alcohol solution was filtered to remove any insoluble impurities and 50% sodium hydroxide solution was then added to the filtrate until the solution was just alkaline to phenolphthalein. A small amount of sulfuric acid may be used to bring the solution to exact neutrality if too much alkali is added. The product may be filtered again to remove any insoluble matter. The solid sodium salt of the alkene-succinic acid, which is a mixture of sodium dodecene-succinates and tridecene-succinates, was obtained by evaporation of the solution. The product is an excellent substantially non-foaming detergent which is especially adapted for use with hard water.

Inasmuch as the above specification comprises preferred embodiments of the invention it is to be understood that the invention is not limited thereto and that changes and modifications may be made therein without departing substantially from the invention, which is defined in the appended claims.

I claim:

1. The method of producing a higher alkene-substituted dicarboxylic acid of the general formula:

\[
\text{R} - \text{C} - \text{COOH} \\
\text{H} - \text{C} - \text{COOH} \\
\text{R}
\]

in which R is selected from the group consisting of hydrogen and alkyl radicals, and Alkene is an alkene group having not less than 5 and not more than 16 carbon atoms, which comprises heating an alkyl halide containing not less than 5 and not more than 16 carbon atoms with an unsaturated aliphatic dicarboxylic acid of the general formula:

\[
\text{R} - \text{C} - \text{COOH} \\
\text{H} - \text{C} - \text{COOH} \\
\text{R}
\]

in which R is selected from the group consisting of hydrogen and alkyl radicals, at a temperature at which hydrogen halide is split out.

2. The method of producing a higher alkene-substituted dicarboxylic acid of the general formula:

\[
\text{R} - \text{C} - \text{COOH} \\
\text{H} - \text{C} - \text{COOH} \\
\text{R}
\]

in which R is selected from the group consisting of hydrogen and alkyl radicals, and Alkene is an alkene group having not less than 5 and not more than 16 carbon atoms, which comprises heating an alkyl chloride containing not less than 5 and not more than 16 carbon atoms with an unsaturated aliphatic dicarboxylic acid of the general formula:

\[
\text{R} - \text{C} - \text{COOH} \\
\text{H} - \text{C} - \text{COOH} \\
\text{R}
\]

in which R is selected from the group consisting of hydrogen and alkyl radicals, at a temperature at which hydrogen chloride is split out.

3. The method of producing an alkene-substituted dicarboxylic acid which comprises heat-
ing a chlorinated kerosene fraction with an un-
saturated aliphatic dicarboxylic acid of the gen-
eral formula:

\[
\begin{align*}
R & - C - COOH \\
& C - COOH \\
& R
\end{align*}
\]

in which \( R \) is selected from the group consisting of hydrogen and alkyl radicals, at a temperature at which hydrogen chloride is split out.

4. The method of producing a higher alkene-
substituted dicarboxylic acid of the general for-
mula:

\[
\begin{align*}
R & - C - COOH \\
& C - COOH \\
& R
\end{align*}
\]

in which \( R \) is selected from the group consisting of hydrogen and alkyl radicals, which comprises heating a tertiary alkyl halide having from 5 to 16 carbon atoms with an unsaturated aliphatic dicarboxylic acid of the general formula:

\[
\begin{align*}
R & - C - COOH \\
& C - COOH \\
& R
\end{align*}
\]

in which \( R \) is selected from the group consisting of hydrogen and alkyl radicals, at a temperature at which hydrogen chloride is split out.

5. The method of producing an alkene-suc-
cinic acid which comprises heating a tertiary
alkyl chloride with maleic anhydride, at a tem-
perature at which hydrogen chloride is split out.

6. The method as defined in claim 1, and fur-
ther characterized in that the reaction is con-
ducted in the presence of an acidic metal halide
catalyst.

7. The method as defined in claim 2 and fur-
ther characterized in that the reaction is con-
ducted in the presence of zinc chloride.

8. The method as defined in claim 5 and fur-
ther characterized in that the reaction is con-
ducted in the presence of zinc chloride.

9. The method of producing an alkene-sub-
stituted dicarboxylic acid which comprises heat-
ing a tertiary alkyl chloride with an unsaturated
aliphatic carboxylic acid of the general formula:

\[
\begin{align*}
R & - C - COOH \\
& C - COOH \\
& R
\end{align*}
\]

in which \( R \) is selected from the group consisting of hydrogen and alkyl radicals, at a temperature at which hydrogen chloride is split out.

10. The method of producing an alkene-sub-
stituted dicarboxylic acid which comprises heat-
ing a chlorinated petroleum fraction obtained by
chlorinating a commercial petroleum fraction
having a boiling range within the range of 190°-
245° C., with an unsaturated aliphatic dicarbox-
ylic acid of the general formula:

\[
\begin{align*}
R & - C - COOH \\
& C - COOH \\
& R
\end{align*}
\]

in which \( R \) is selected from the group consisting of hydrogen and alkyl radicals, at a temperature at which hydrogen chloride is split out.

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