Aug. 5, 1969 A. SZCZEPANEK ETAL **3,459,776**

PROCESS FOR THE PRODUCTION OF METAL SOAPS OF
EPOXYDIZED FATTY ACIDS
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FIG. 2.

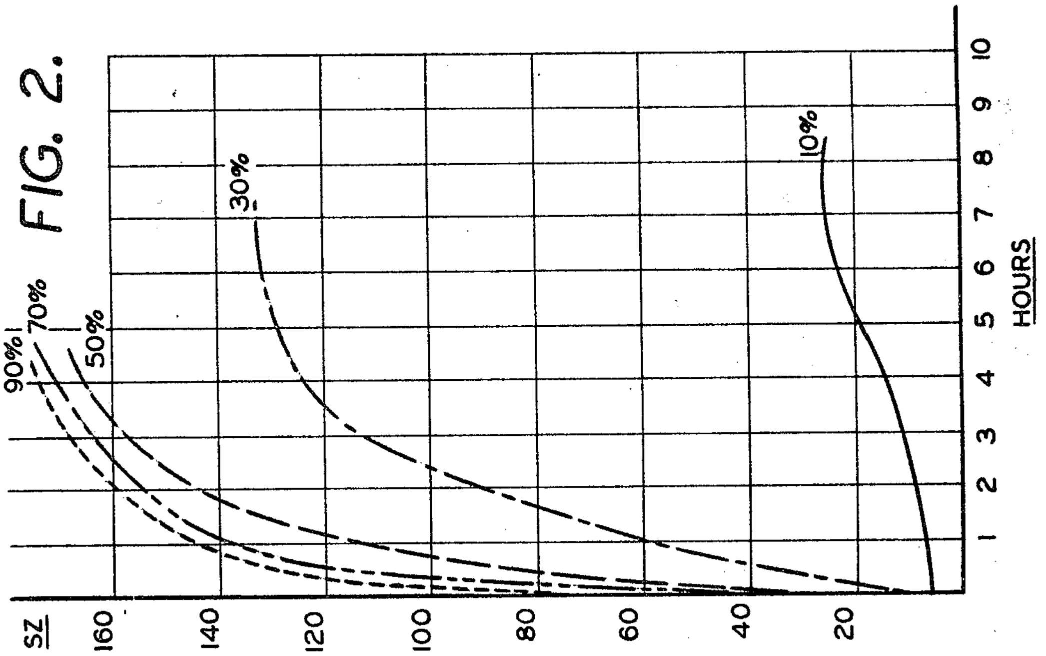
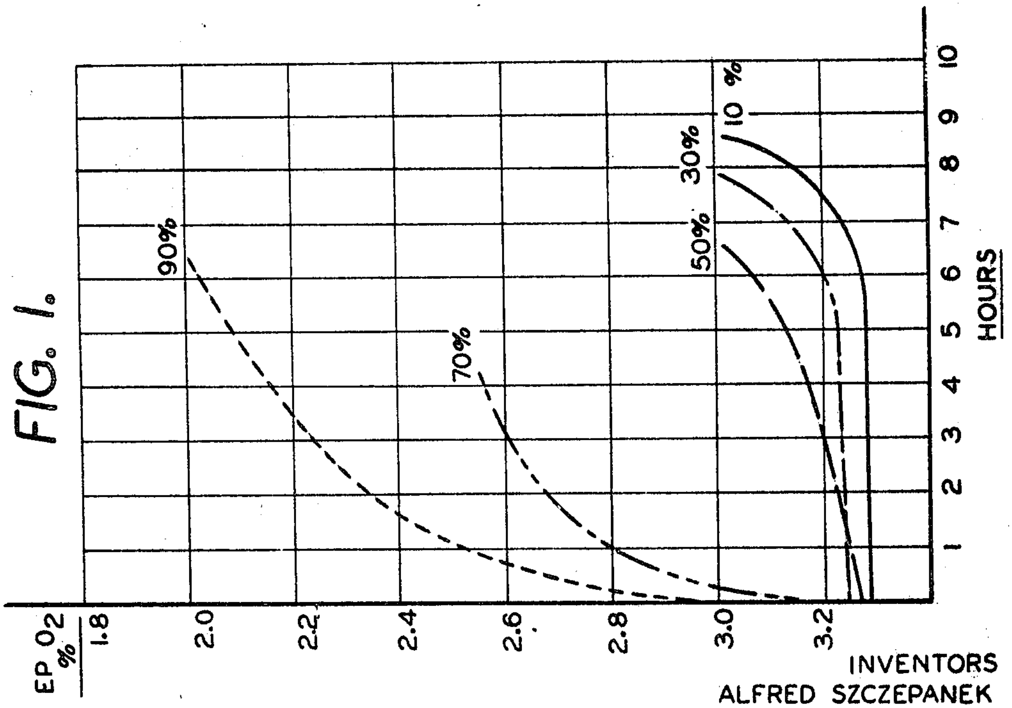


FIG. 1.



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PROCESS FOR THE PRODUCTION OF METAL SOAPS OF EPOXYDIZED FATTY ACIDS

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Continuation-in-part of application Ser. No. 114,293, June 2, 1961. This application Apr. 1, 1964, Ser. No. 356,473

Claims priority, application Germany, June 3, 1960, C 21,597

Int. Cl. C07f 7/24, 5/06, 3/00

U.S. Cl. 260—348 8 Claims

The present invention is concerned with the process for the production of metal soaps of epoxidized fatty acids.

This application is a continuation-in-part of application Ser. No. 114,293, filed June 2, 1961, now abandoned.

Metal soaps of epoxidized fatty acids have frequently been proposed for the heat and light stabilizing of halogen-containing synthetic resins.

It is known that metal soaps of saturated and unsaturated fatty acids can be produced by the following processess;

(a) Double reaction between a water-solution alkali metal or ammonium soap of the fatty acids and a water-soluble metal salt;

(b) Reaction of fatty acids with metal oxides, hydroxides, and salts of volatile acids in the melt.

These known processes cannot be used for the production of metal soaps of epoxidized fatty acids without the use of special measures. The epoxy ring is very labile with regard to water, aqueous alkalis and acids, especially at elevated temperatures, whereby glycols or glycol derivatives are formed. Furthermore, epoxy compounds in the presence of certain metal salts have a tendency to polymerize.

In British patent specification No. 754,854, there is described a process for producing metal soaps of epoxidized fatty acids by the neutralization of epoxy fatty acids with alkali at room temperature in an aqueous medium and subsequent precipitation with water-soluble metal salts using the process described above under (a). However, in repeating the process under the described conditions, we found that the products so obtained are not homogeneous and contain considerable amounts of starting material and intermediate products which impairs the usefulness of the epoxy metal soaps.

The saponification of the epoxy fatty acids which are not liquid at room temperature, for example, epoxy stearic acid, with sodium hydroxide in an aqueous medium is incomplete, even with vigorous dispersion and long reaction time, so that the end products are contaminated, after the precipitation, with large amounts of epoxy fatty acid. Furthermore, large amounts of alkali metal soaps are entrained during the precipitation which can only be removed from the reaction product with great difficulty.

The epoxy fatty acids, which are liquid or semi-liquid at room temperature, for example, diepoxy-stearic acid, can admittedly be easily saponified at room temperature in an aqueous medium with alkalis in the same manner as their starting substance, linoleic acid, but, nevertheless, the epoxy metal soaps obtained after the precipitation are considerably contaminated with the alkali metal soaps. Corresponding to the unreacted free epoxy fatty acid, there results from the amount of alkali metal hydroxide equivalent hereto by the precipitation with the metal salts, metal hydroxides which, as a result of the their insolubility cannot subsequently be removed by washing and lead to a clouding of the transparent polyvinyl chloride.

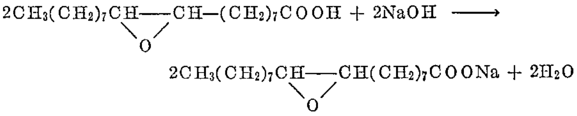
In the case of some fields of application, alkali metal soaps have an undesired effect by increasing the take up of water, together with an increase of the conductivity and cloudiness.

A further teaching in the prior art is contained in British Patent 825,691. This patent teaches a procedure for making divalent soaps of epoxidized fatty acids, the procedure involving starting with an ester, in particular the epoxidized glyceride or oil, contacting the ester alkali metal hydroxide in an ethanol medium containing a small proportion of water, namely about 10–20% water. This process has the disadvantage of involving destruction of the epoxy groups to an objectionable extent. Further, it has the limitation that the ester of the epoxy fatty acid must be used as starting material.

The object of the present invention is a process of good reproducibility, in which, while preserving the epoxy group, the production of metal soaps of epoxy fatty acids is possible, said soaps being substantially free from starting materials and intermediate products. According to the present invention, the metal soaps of epoxydized fatty acids are obtained by the double reaction of their alkali metal or ammonium salts with-soluble metal salts. An important factor for the preservation of the epoxy group is the maintenance of a low reaction temperature and a short saponification time for the conversion of the epoxy fatty acids or their esters into the alkali metal or ammonium soaps.

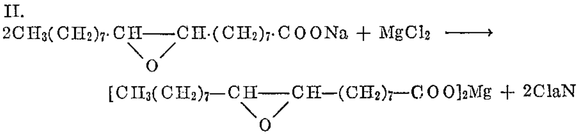
The process takes place in two steps. For example, in the first step, alkali metal soaps are produced by the reaction of epoxidized fatty acids or their esters or glycerides with an aqueous alcoholic solution of alkali metal hydroxides, the alkali metal soaps thus produced then being reacted in a second step with a water-soluble metal salt. In the case of epoxy-stearic acid and magnesium chloride, the reaction takes place according to the following equation:

I.



$$2\mathrm{CH_3(CH_2)_7}\underset{\diagdown\,\mathrm{O}\,\diagup}{\mathrm{CH{-\!-}CH}}\mathrm{-(CH_2)_7COOH} + 2\mathrm{NaOH} \longrightarrow 2\mathrm{CH_3(CH_2)_7}\underset{\diagdown\,\mathrm{O}\,\diagup}{\mathrm{CH{-\!-}CH}}\mathrm{(CH_2)_7COONa} + 2\mathrm{H_2O}$$

II.



$$2\mathrm{CH_3(CH_2)_7\cdot}\underset{\diagdown\,\mathrm{O}\,\diagup}{\mathrm{CH{-\!-}CH}}\mathrm{\cdot(CH_2)_7\cdot COONa} + \mathrm{MgCl_2} \longrightarrow [\mathrm{CH_3(CH_2)_7{-}}\underset{\diagdown\,\mathrm{O}\,\diagup}{\mathrm{CH{-\!-}CH}}\mathrm{-(CH_2)_7{-}COO}]_2\mathrm{Mg} + 2\mathrm{ClaN}$$

In the case of the known production of metal soaps, the saponification of fatty acids with alkali metal hydroxides, is, in general, carried out at a temperature above the melting point of the acid and in a concentration which is determined by the solubility of the alkali metal soap. In this case, one uses temperatures which are as high as possible and which are dependent upon the melting point of the metal soaps produced, in order to limit the amount of water necessary and in order to increase the throughput rate per reaction vessel. These reaction conditions cannot be applied to the production of alkali metal soaps of epoxy fatty acids since the epoxy group is split off in an alkali medium at an elevated temperature. Therefore, the reaction with alkali metal hydroxides according to the present invention is preferably carried out at room temperature. As reaction media there are used organic solvents miscible with water, in the form of solutions thereof with water. The preferred organic solvents are alcohols.

With respect to production of the salts, starting with the fatty acids, the invention comprises contacting epoxidized fatty acid in an aqueous, organic liquid, alkaline medium with a monovalent cation for saponification to form salt of the epoxidized fatty acid and the cation, and thereafter contacting the salt with an aqueous solution of a water-soluble salt of the polyvalent metal to be produced, to thereby form the polyvalent metal soap product.

With respect to production of the metal soaps starting with the fatty acids or fatty acid esters, and particularly with respect to the use of fatty acid esters as starting material, an aqueous, organic liquid medium for the first step wherein the saponification is performed, is preferred.

With respect to the use of aqueous, organic liquid means in the first step, it has been found, suprisingly, that in effectiveness of the process having particular regard for production with little destruction epoxy groups, the proportion of organic liquid to water is important. The importance of the concentration of the organic liquid is illustrated by the accompanying graphs, wherein:

FIG. 1 is a graph of time in hours versus the percentage of epoxy groups in the product, with the percent organic liquid as parameter, the organic liquid being ethanol; and

FIG. 2 is a graph of time versus acid number with a parameter as is the case in FIG. 1, and also for ethanol as the organic liquid.

The graph of FIG. 1 shows the decrease of the epoxy-oxygen in dependence on time, with the alcoholic content of the solution used as parameter. Decrease in oxygen of the epoxy group is light in alcoholic solutions of up to about 50% (that is, is slight for the curves for 10%, 30% and 50%), but rises sharply in the case of 70% alcohol and more concentrated alcoholic solutions in the desired operating times of 2–4 hours.

The graph of FIG. 2 shows the increase in acid number in dependence on time, the strength of the aqueous alcoholic solutions being again shown as parameter. A high acid number shows that the saponification proceeds rapidly in the desired time. For the desired rapid reaction, an alcoholic concentration of at least about 50% is preferred.

The dependence of the variables involved, as is indicated in FIG. 1, is generally true for the process of the invention for the acid and esters as starting materials. FIG. 2 shows dependence of the variables when the starting material is the ester. Thus, the invention provides a procedure permitting the production of the epoxy metal soaps with little destruction of the epoxy groups by suitable selection of the reaction conditions, particularly the concentration of the organic liquid in the medium employed.

In the figures and throughout the specification and claims, unless otherwise indicated, the concentration of organic liquid is percent of organic liquid based on the organic liquid and water.

The organic solvents used must be at least partially water-soluble and possess a good dissolving power not only for the epoxidized compounds serving as starting materials but also for their alkali metal soaps. The most suitable solvents are the aliphatic C_1–C_4 branched and straight chain alcohols. Ethanol is preferred. The ratio water:alcohol is dependent not only upon the nature of the alcohol, but also of the reaction components.

Broadly, the organic liquid content of the medium for the first step can be about 10–70% organic liquid, for example 10–70% alcohol.

With respect to the use of ester, and also the use of acid, as starting material, in general, at low temperature a high content of organic liquid can be used, and as the temperature is increased, the content of alcohol or other organic should be decreased. Thus, at room temperature, an organic liquid content, for example an alcohol content, and in particular an ethanol content, of 50–70% is preferred, whereas at 50° the said content is preferably 20–50%. If high organic liquid content is used at high temperature, the destruction of epoxy groups becomes faster than the saponification. Thus, the organic liquid content of the medium is an important factor in realization of suitable saponification rates and suitable retention of epoxy groups. In some cases, production of the product desired will not be realized in the absence of the selection of appropriate organic liquid concentration-temperature relationship.

As a general rule, for selection of a suitable organic liquid concentration-temperature relationship, the reaction temperature for the saponification can be between room temperature and about 60° C., the alcohol content of the medium should correspond to the saponification temperature to provide retention of epoxy groups at least equal to that obtained for the saponification at a temperature of 50° C. and an alcohol content of 30%.

The saponification of the epoxy fatty acid ester is an equilibrium reaction, depending upon temperature and time, in which the saponification and ring opening of the epoxy group proceed simultaneously.

At room temperature and in aqueous alcoholic medium the saponification velocity of the ester is considerably higher than the ring opening velocity of the epoxy group. For the obtaining of metal soaps with a high epoxy oxygen content is is, therefore, important to maintain a suitable reaction time at which the saponification is as complete as possible and in which the epoxy ring opening is substantially suppressed. The reaction time is dependent upon the nature of the ester and the ratio or water to alcohol. For methyl esters, the saponification time amounts to about 0.5 hour and for esters of polybasic alcohols to 2 to 4 hours. In general reaction time is about 0.5–4 hours. The ratio of water to alcohol is, as already mentioned, dependent upon the nature of the ester, of the alcohol and of the solubility of the alkali metal soap formed in the saponification mixture. Furthermore, in the case of certain metal soaps, the degree of polymerization is also influenced.

The dependence of the polymerization of the metal soaps upon the ratio of alcohol to water is particularly noticeable in the case of the saponification of the zinc soaps from epoxidized linseed fatty acid. These soaps can be produced in aqueous alcoholic solution with an ethanol content of more than 50% without difficulty but, in the case of an alcohol content below 50%, products are obtained which, in the case of the epoxy oxygen determination, can no longer be decomposed with hydrochloric acid ether.

Because of the economics of the process, it is advisable to work with the smallest possible amount of alcohol. In general, the alcohol or other organic liquid content of the aqueous solution amounts to 10–70%, preferably 50–70%, or better 50–60%, and is so chosen that the alkali metal soaps formed are clearly soluble. In the case of acids as starting material, a good range or organic liquid, e.g. alcohol, concentration is about 10–60%. The lowest limit of the alcohol content of the saponification mixture amounts to 10% in the case of the epoxidation products of poly-unsaturated acids. Since the saponification does not proceed to completion, the metal soaps of epoxy fatty acids produced according to this process contain small amounts of starting esters which, according to the intended use, are either washed out with organic solvents or, for example, for use as polyvinyl chloride stabilizers, are not disturbing since the epoxydized esters of fatty acids are valuable plasticizers.

The alkaline material used to provide the desired alkaline conditions can be any suitable alkaline material. Instead of alkali metal hydroxides, one can also use alkali metal oxides, metallic oxides or hydroxides which form soluble epoxy metal soaps in the reaction mixture, or ammonium hydroxide or its derivatives. In the case of acids as starting material the alkali metal alcoholates can be used. For the saponification, it is preferred to use the oxides, hydroxides and alcoholates, of Group I of the Periodic System, ammonium hydroxides and its derivatives. In principal, it is also possible to use other basically reacting metal compounds when the metal soaps formed are soluble in the water-alcohol mixture, Potassium and sodium hydroxide are preferred by reason of more rapid reaction.

Esters with mono- or polybasic alcohols can be converted in the saponification to metal soaps. The esters can be produced by the trans-esterification of unsaturated naturally occurring oils and, if desired, purified by fractional distillation. Glycerides, glycol derivatives, etc. can be employed. Where the ester is an ester of a monobasic alcohol, the alcohol can be a lower alkanol having about 1–4 carbon atoms. The alcohol, however, can be a higher alcohol. In general, the aliphatic alcohols can provide the alcohol moiety of the ester.

The epoxy values of epoxydized fatty acids, in contradistinction to their esters, decreases very rapidly upon storage, presumably because the presence of the carboxylic acid group opens the epoxy ring. The technical application of epoxydized fatty acids is thereby rendered difficult.

The use of esters renders possible the production of metallic soaps of epoxy-ricinolic acid while avoiding the technically difficult isolation and purificaton of the ricinolic acid.

The rapid saponification of epoxydized esters by aqueous alcoholic alkalis at room temperature is surprising and was not to be expected since the non-epoxydized esters under these reaction conditions are not or only very slightly saponifiable. The introduction of an epoxy group into a fatty acid ester considerably increases its saponification velocity.

Epoxydized fatty acids and their esters as starting materials in the sense of the present invention are the products produced by known processes, preferably from naturally occurring unsaturated fatty acids or their esters. They contain the by-products formed by the opening of the ring of the epoxy group in the epoxydation but the use of pure starting material is also possible in principal. In general, the fatty acid or the fatty acid moiety can contain about 11–22 carbon atoms. Preferred starting materials are epoxydized undecylenic acid, oleic acid, linoleic acid and linolenic acid, either alone or in admixture with one another or with saturated fatty acids, as well as the esters of mono- or polybasic alcohols, such as methanol and glycol, obtained therefrom, and the glycerides of these acids.

By epoxydized fatty acids is meant fatty acids containing oxirane rings. There can be one or more than one epoxy group present.

A further advantage of the saponification with aqueous alcoholic alkali metal hydroxide solutions is that the crude products obtained after the epoxydation of unsaturated fatty acids and of their esters can be converted into the metal soaps via the alkali metal soaps without working up.

The reaction of the alkali metal soaps to the metal soaps takes place by the addition of an aqueous solution of the corresponding metallic salt at room temperature. The usually powdery products are filtered off, freed from the alkali metal salts formed during the reaction by washing with water and carefully dried at temperatures of 50–60° C.

As metal components there are suitable all metals which form metallic soaps with fatty acids. The metal can be a metal of Group II–IV, particularly the following metals: sodium, lithium, magnesium, aluminum lead, calcium, barium, cadmium, zinc and manganese.

For the characterization of the metal soaps the metal content, epoxy oxygen value, melting point and free fatty acid were determined. For the determination of the characterizing data, generally known methods are used, apart from the determination of the epoxy oxygen content of the epoxy metal soaps. As a result of the insolubility of the epoxy metal soaps in the usual solvents used for the determination of the epoxy oxygen value, this value cannot be determined directly. The metal soap is decomposed, down to the complete decomposition of the soap, at lower temperatures in the presence of ether with 2 N hydrochloric acid. The ethereal solution is subsequently washed with water, dried over anhydrous sodium sulphate and distilled off at a low temperature. The epoxy oxygen value is then determined by the known method on the isolated epoxy fatty acid. Control tests with epoxy- and diepoxy-stearic acid show that the test conditions used for the decomposition of the epoxy metal soaps only lead to a negligible reduction of the epoxy oxygen content of the epoxy fatty acid so that this indirect method for the determination of the epoxy oxygen content of the epoxy metal soaps gives a substantially correct value.

The following Table I gives a summary of the physical constants of the epoxy starting materials.

TABLE I

Substance	Iodine number of starting material	Epoxy oxygen, percent	Epoxydized compound		
			Iodine number	Acid number	Saponification number
Epoxydized undecylenic acid	152	2.6–5.2	2–5	250	----------
Epoxydized methyl ester of undecylenic acid	140	3.7–5.6	2.5	----------	250–260
Epoxydized oleic acid	90	2.7–4.5	1.5	174–182	----------
Epoxydized methyl ester of oleic acid	90–94	3.7–4.6	0.3–3.0	0.5–4	190–191
Epoxydized linseed oil fatty acid	174	5.3–6.7	2–5	175–185	----------
Epoxydized methyl ester of linseed oil fatty acid	160	5.3–6.4	1–6	----------	177–189
Epoxydized soyabean oil	150	5.9	10.4	----------	182
Epoxydized castor oil	52	3.9	2	3	180
C20–C22 acid mixture	197	3.8–5.0	3–5	155–180	----------
Epoxydized methyl ester of C_{20}–C_{22} acid mixture	190	4.4–5.5	3–5	----------	150–170
Epoxydized olive oil	95	4.2	1	1	184
Epoxydized linseed oil	190	7.0–7.5	1–2	3.1	186

The impurities or by-products contained in these technical products influence the physical constants of the metallic soaps produced therefrom but are, however, of no significance for the preferred technical use as polyvinyl chloride stabilizers. The products produced according to the invention consist mainly of the metal soaps of the following acids: 10,11-epoxy-undecanic acid, 9,10-epoxy-stearic acid, 9,10,12,13-diepoxy-stearic acid, 9,10,15,16-diepoxy-Δ-12,13-stearic acid, 9,10,12,13,15,16-triepoxy-stearic acid and the epoxydation products of polyunsaturated C_{20}–C_{22} fatty acids obtained from fish oils.

The melting range and appearance of the metal soaps produced are to be seen from the following tables.

TABLE II.—METAL SOAPS OF EPOXYDIZED UNDECYLIC ACID

Metal	Type	Melting range, ° C.	Appearance
Barium	di	161–166	White powder.
Calcium	di	106–114	Do.
Cadmium	di	152–178	Do.
Magnesium	di	86–96	Do.
Sodium	mono	150–190	Do.
Manganese	di	122–135	Red-brown, coarse grained powder.
Zinc	di	114–118	White powder.

TABLE III.—METAL SOAPS FROM EPOXYDIZED METHYL ESTER OF UNDECYLENIC ACID

Metal	Type	Melting range, ° C.	Appearance
Barium	di	153–157	White powder.
Calcium	di	102–118	Do.
Cadmium	di	110–118	Do.
Manganese	di	85–101	Brownish-black plastic.
Sodium	mono	160–205	White powder.
Zinc	di	108–128	White, easily plastic powder.

TABLE IV.—METAL SOAPS FROM EPOXYDIZED OLEIC ACID

Metal	Type	Melting range, ° C.	Appearance
Barium	di	120–141	Yellowish powder.
Calcium	di	97–105	Yellowish, easily plastic powder.
Cadmium	di	84–150	Yellowish sintered powder.
Magnesium	di	98–115	Voluminous white powder.
Sodium	mono	160–200	White powder.
Manganese	di	87–139	Pink, easily sintered powder.
Zinc	di	90–98	Sintered powder.
Aluminum	mono	(1)	White powder.
Do	di	(2)	Do.
Do	tri	(3)	Yellowish, easily plastic.
Lead	dibasic di	(1)	Yellowish powder.
Do	di	70–102	Light yellow, easily plastic.

[1] Above 200°.
[2] 70° sinters, up to 200° no clear melting.
[3] 45° sinters, up to 200° no clear melting.

TABLE V.—METAL SOAPS OF EPOXYDIZED METHYL ESTER OF OLEIC ACID

Metal	Type	Melting range, ° C.	Appearance
Barium	di	85–126	Yellowish, easily plastic powder.
Calcium	di	93–115	White, easily plastic powder.
Cadmium	di	90–166	Do.
Magnesium	di	83–89	Yellowish, plastic mass.
Manganese	di	82–158	Dark brown plastic.
Sodium	mono	>200	White powder.
Zinc	di	90–105	White, easily plastic powder.
Lithium	mono	>200	White powder.

TABLE VI.—METAL SOAPS OF EPOXYDIZED LINSEED OIL FATTY ACID

Metal	Type	Melting range, ° C.	Appearance
Barium	di	137–141	Yellowish, easily plastic powder.
Calcium	di	98–110	Yellowish, granular powder.
Cadmium	di	81–181	White powder.
Magnesium	di	105–110	White, easily plastic powder.
Manganese	di	72–83	Whitish-pink, easily sintered powder.
Sodium	mono	167–195	Yellowish, easily plastic powder.
Zinc	di	103–107	White, plastic powder.
Aluminum	mono	(1)	White powder.
Do	di	(2)	Light yellowish, easily plastic powder.
Do	tri	(3)	Yellowish, plastic.
Lead	di	90–128	Brownish, plastic.
Do	dibasic di	(1)	Yellowish powder.

[1] Above 200°.
[2] 65° sinters, up to 200° no clear melting.
[3] 40° sinters, up to 200° no clear melting.

TABLE VII.—METAL SOAPS FROM EPOXYDIZED METHYL ESTER OF LINSEED OIL FATTY ACID

Metal	Type	Melting range, ° C.	Appearance
Barium	di	123–138	Yellowish, sintered powder.
Calcium	di	88–90	White, plastic.
Cadmium	di	170–179	White powder.
Magnesium	di	89–93	White, somewhat plastic powder.
Sodium	mono	80–178	Whitish-yellow, slightly plastic powder.
Zinc	di	70–110	Yellowish plastic.

TABLE VIII.—METAL SOAPS FROM EPOXYDIZED SOY BEAN OIL

Metal	Type	Melting range, ° C.	Appearance
Barium	di	107–122	Yellowish plastic.
Calcium	di	88–135	Do.
Cadmium	di	155–172	Do.
Magnesium	di	66–102	Whitish-yellow, plastic mass.
Zinc	di	77–158	Yellowish plastic.

TABLE IX.—METAL SOAPS FROM EPOXYDIZED CASTOR OIL

Metal	Type	Melting range, ° C.	Appearance
Calcium	di	85–100	White, easily plastic powder.
Cadmium	di	152–155	Do.
Magnesium	di	----------	White plastic mass.
Sodium	mono	91–120	Yellowish powder.
Zinc	di	105–115	Light yellowish, plastic
Aluminum	mono	(1)	White powder.
Do	di	(1)	White powder, easily plastic.
Do	tri	(1)	Do.
Lead	dibasic di	(2)	Yellow, plastic.

[1] Above 200°.
[2] 136° sinters up to 200° no clear melting.

TABLE X.—METAL SOAPS FROM EPOXYDIZED C_{20}–C_{22} ACID MIXTURE

Metal	Type	Melting range, ° C.	Appearance
Barium	di	68–144	Whitish-yellow, granular powder.
Calcium	di	95–175	Yellowish, granular powder.
Cadmium	di	81–89	White powder.
Magnesium	di	80–86	Yellowish, somewhat plastic powder.
Manganese	di	72–76	Pink, easily sintered powder.
Sodium	mono	112–170	Yellowish, easily sintered powder.
Zinc	di	92–104	Whitish-yellowish, plastic.

TABLE XI.—METAL SOAPS FROM EPOXYDIZED METHYL ESTERS OF C_{20}–C_{22} ACID MIXTURE

Metal	Type	Melting range, ° C.	Appearance
Barium	di	90–140	White, plastic.
Calcium	di	65–85	Yellowish-white, easily plastic powder.
Cadmium	di	164–180	Yellowish, easily sintered powder.
Magnesium	di	72–88	Yellowish-white, plastic mass.
Manganese	di	84–138	Brown-black, plastic.
Zinc	di	88–200	Yellowish plastic.
Sodium	mono	155–210	White, granular powder.

TABLE XII.—METAL SOAPS FROM EPOXYDIZED OLIVE OIL

Metal	Type	Melting range, ° C.	Appearance
Calcium	di	90–95	White powder.
Cadmium	di	125–147	White, easily sintered powder.
Zinc	di	77–120	White powder.

TABLE XIII.—METAL SOAPS FROM EPOXYDIZED LINSEED OIL

Metal	Type	Melting range, ° C.	Appearance
Calcium	di	88–91	Brownish plastic.
Cadmium	di	95–158	Yellowish, easily plastic powder.
Zinc	di	62–90	Do.

Sodium and potassium soaps based upon epoxydized undecylenic acid and epoxydized oleic acid are white crystalline powders with a melting point of 160–200° C. On the other hand, the products obtained, for example, from epoxydized linseed fatty acid or epoxydized castor oil are readily adhering powders which are somewhat yellowish in color and have a melting range between 150–200° C. The solubility of the sodium and potassium epoxy soaps in water increases, by equal chain length, with the increasing number of epoxy groups.

The possibility of producing the lithium soaps of epoxy fatty acids is shown in the following, based on the example of the epoxydized methyl ester of oleic acid, from which can be produced lithium epoxy stearate using lithium hydroxide in water-alcohol mixture. It is a white crystalline powder with a melting point of over 200° C.

The partially considerably water-soluble magnesium soaps of the epoxy fatty acids are obtained, by double reaction of their alkali metal soaps with magnesium chloride, as white powders or white to yellowish plastic masses with a melting range of 70–120° C. Their tendency to polymerize with loss of the epoxy oxygen content is considerable, the crystalline magnesium epoxy soaps going over into a plastic state.

The calcium soaps of the epoxy fatty acids are white, crystalline to yellowish readily plastic powders with a melting range of 85–120° C. Their water solubility, with the exception of calcium soap of epoxy linseed fatty acid, is slight, as is also their tendency to polymerize with the splitting off of the epoxy group.

The barium soaps of the epoxydized fatty acids are white crystalline to yellowish, readily plastic, frequently very water soluble substances with a melting range between 100 and 160° C. The tendency of the epoxy group to polymerize is slight.

The cadmium soaps of the epoxydized fatty acids are white crystalline to yellowish readily plastic powders with a melting range between 100 and 180° C. Their water solubility is, in general, slight, as is their tendency to polymerize with the reduction of the epoxy oxygen content.

The zinc soaps of the epoxydized fatty acids are white crystalline to yellowish plastic products with a melting range between 100 and 120° C. Their water solubility is slight and the tendency to polymerize exists only in the case of epoxydized castor oil.

The manganese soaps of the epoxydized fatty acids are pink to red-brown colored crystalline to plastic products with a melting range of between 80 and 130° C. Their tendency to polymerize is light.

The mono-, di- and tri-aluminum soaps of epoxylized fatty acids can be produced by the reaction of the alkali metal soaps with aluminum sulphate. They are white to pale yellow somewhat sticky powders, whose lower epoxy oxygen content indicates a splitting off of the epoxy group either by polymerization or by the acidic reaction of the aluminum sulphate solution.

Normal and basic lead epoxy soaps can be produced by the double reaction of the alkali metal soaps with lead acetate. They are white-yellowish crystalline to plastic products which have a strong tendency to polymerize with loss of the epoxy oxygen content.

The following examples are given for the purpose of illustrating the present invention:

Example 1.—Cadimium soap of epoxydized methyl ester of undecylenic acid

21.4 g. epoxydized methyl ester of undecylenic acid (EpO_2 4.5%) are dissolved in 150 ml. 96% ethanol and 4 g. sodium hydroxide in 80 ml. water added thereto at room temperature. One stirs for half an hour at room temperature until the solution has become clear and adds, with stirring, 73 g. of a cadmium nitrate solution (=5.7 g. cadmium), which contains 78 g. cadmium per kg. One adds three times the volume of water and stirs for a further two hours at room temperature for the purpose of completion of the precipitation. After filtration and washing, the product is dried at 50° C. Yield 24 g.=94% of the theory, cadmium 21.5%, melting point 110–188° C., epoxy oxygen of the isolated acid 4.6%.

Example 2.—Di-aluminum soap of epoxydized oleic acid

62.4 g. epoxydized oleic acid (EpO_2 2.8%) are dissolved in 300 ml. 96% ethanol and 12 g. sodium hydroxide in 240 ml. water added at room temperature. One stirs for half an hour at room temperature until the solution has become clear, adds, with stirring, 33.9 g. aluminum sulphate octadecahydrate in 200 ml. water, adds a further 300 ml. water thereto and subsequently stirs for a further hour. After filtration and washing, the product is dried at 60° C. Yield 70 g., aluminum 4.84%, melting range 70–200° C., epoxy oxygen of the isolated acid 0.53%.

Example 3.—Dibasic lead soap from epoxydized oleic acid

31.2 g. epoxydized oleic acid (EpO_2 2.92%) are dissolved in 300 ml. 96% ethanol and 12 g. sodium hydroxide in 240 ml. water added thereto at room temperature. One stirs for half an hour at room temperature until the solution has become clear and adds thereto, with stirring, 58 g. lead acetate trihydrate in 300 ml. water, adds a further 300 ml. water thereto and subsequently stirs for a further hour. After filtering and washing, the product is dried at 60° C. Yield 47 g. lead 44.9%, melting point 70–102° C., epoxy oxygen of the isolated acid 2.98%.

Example 4.—Manganese soap of epoxydized methyl ester of oleic acid

31.2 g. epoxydized methyl oleate (EpO_2 3.3%) are dissolved in 150 ml. 96% ethanol and 4 g. sodium hydroxide in 80 ml. water added thereto, with stirring, at room temperature. One stirs for half an hour until a clear solution is obtained and adds 10.4 g. manganese acetate trihydrate thereto as an aqueous solution. One adds three times the volume of water and stirs for a further two hours for the purpose of completion of the precipitation. After filtration, the product is dried at 503° C. Yield 32 g.=99% of theory, manganese 7.2%, melting point 82–158° C., epoxy oxygen of the isolated acid 3.6%.

Example 5.—Zinc soap of epoxydized linseed fatty acid

15.6 g. epoxydized linseed fatty acid (EpO_2 4.3%) are dissolved in 75 ml. ethanol and 2 g. sodium hydroxide in 40 ml. water added thereto with stirring. One stirs for half an hour at room temperature until the solution has become clear, adds thereto 7.3 g. zinc sulphate as an aqueous solution, dilutes with three times the volume of water, allows to stand for 60 hours and filters. The product is dried at 50° C. Yield 17 g.=99% of theory, zinc 10.1%, melting point 103–107° C., epoxy oxygen of the isolated acid 3.2%.

Example 6.—Cadmium soap of epoxydized linseed fatty acid methyl ester

32.4 g. epoxydized linseed acid methyl ester (EpO_2 6.2%) are dissolved in 150 ml. 96% ethanol and 4 g. sodium hydroxide in 80 ml. water added thereto at room temperature with stirring. One stirs for about half an hour until the solution has become clear and then adds thereto 6.73 g. of a cadmium nitrate solution (=5.7 g. cadmium) which contains 78 g. cadmium per kg. After dilution with three times the volume of water, one stirs for a further two hours and filters. The product is dried at 50° C. Yield 37.5 g.=97.5% of theory, cadmium 15.6%, epoxy oxygen of the isolated acid 5.4%, melting point 170–179° C.

Example 7.—Magnesium soap of epoxydized soybean oil

32.2 g. apoxydized soybean oil (epoxy oxygen 5.2%) are dissolved in 150 ml. 96% ethanol and 4 g. sodium hydroxide dissolved in 80 ml. water added with stirring at room temperature. One stirs for about half an hour until the solution has become clear and adds thereto 10.4 g. magnesium chloride dissolved in water. After dilution to three times the volume with water, one stirs for two hours and filters off. The product is dried at 50° C. Yield 27 g., magnesium 3.1%, epoxy oxygen of the isolated acid 5.6% melting point 66–102° C.

Example 8.—Cadmium soap from epoxydized castor oil

200 g. epoxydized castor oil (EpO_2 4.6%) are dissolved in 925 ml. 96% ethanol and 24.8 g. sodium hydroxide in 495 ml. water added thereto, with stirring, at room temperature. One stirs for about half an hour, then adds 97 g. cadmium nitrate tetrahydrate in about 500 ml. water thereto, dilutes at the end of the precipitation with about 1.5 liters water, again stirs for two hours, filters, washes and dries at about 60° C. Yield 223 g., cadmium 13.4%, melting point 157–165° C., epoxy oxygen of the isolated acid 4.05%.

Example 9.—Barium soap of epoxydized C_{20}–C_{22} acid mixture

15 g. epoxydized C_{20}–C_{22} acid mixture (EpO_2 3.2%) are dissolved in 62 ml. 96% ethanol and 1.74 g. sodium hydroxide in 32 ml. water added thereto, with stirring, at room temperature. One stirs for about half an hour until the solution has become clear and then adds 5.4 g. barium chloride dihydrate as aqueous solution. After dilution with three times the volume of water, one stirs for two hours at room temperature and filters off the product. Drying at 50° C., yield 14 g.=78% of theory, barium 17.0%, melting point 68–144° C., epoxy oxygen of the isolated acid 2.8%.

Example 10.—Calcium soap of epoxydized methyl ester of C_{20}–C_{22} acid mixture

30 g. epoxydized methyl ester of C_{20}–C_{22} acid mixture (EpO_2 4.7%) are dissolved in 124 ml. 96% ethanol and 3.3 g. sodium hydroxide in 66 ml. water added thereto, with stirring, at room temperature. One stirs at room temperature for about half an hour until a clear solution has been formed and then adds 5.2 g. calcium chloride (91%) as an aqueous solution. After dilution with three times the volume of water, one stirs at room temperature for a further two hours, filters off the product, washes and dries at 50° C. Yield 32 g., calcium 5.0%, epoxy oxygen of the isolated acid 4.2%., melting point 65–85° C.

Example 11.—Calcium soap of epoxidized olive oil

29.8 g. epoxydized olive oil (EpO_2 4.0%) are dissolved in a mixture of 100 ml. 96% ethanol and 55 ml. butanol and 4 g. sodium hydroxide in 80 ml. water added thereto at room temperature with stirring. One warms to 30° C. and continues stirring for up to half an hour until a clear solution is obtained 6.2 g. calcium chloride (91%) dissolved in 300 ml. water are then added, with stirring. After dilution with three times the volume of water, one stirs for two hours, filters off the product, washes and dries at 50° C. Yield 30.5 g., calcium 4.6%, melting point 90–95° C., epoxy oxygen of the isolated acid, 3.6%.

Example 12.—Zinc soap of epoxidized linseed oil

28.6 g. epoxydized linseed oil (EpO_2 6.5%) dissolved in 150 ml. ethanol and 4 g. sodium hydroxide dissolved in 80 ml. water added thereto with stirring. One stirs for half an hour at room temperature and then adds 14.65 g. zinc sulphate dissolved in 300 ml. water. The product is filtered off, washed and dried at 50° C. Yield 28 g., zinc 9.8%, melting point 62–90° C., epoxy oxygen of the osolated acid 6.3%.

What is claimed is:

1. Process for the prouction of polyvalent metal soaps of epoxidized fatty acids, which comprises:
   (a) contacting epoxidized fatty acid in an aqueous, alcoholic, alkaline medium with a monovalent metal cation for saponification to form the salt of the epoxidized fatty acid and said cation, said medium being a solvent for the epoxidized fatty acid and said salt, and containing about 10–70% alcohol based on the alcohol and water present therein, and
   (b) contacting said salt with an aqueous solution of a water soluble salt of the said polyvalent metal to form said polyvalent metal soap.

2. Process according to claim **1**, said medium containing an alkaline material selected from the group consisting of alkali metal oxides, alkali metal hydroxides and alkaline ammonium compounds, said alkaline material rendering the medium alkaline and providing said monovalent cation.

3. Process according to claim **1**, said alcohol content being 10–60%.

4. Process according to claim **1**, said medium containing alkali hydroxide, said alkali hydroxide rendering the medium alkaline and providing said monovalent cation.

5. Process according to claim **1**, said contacting being at room temperature, said aqueous alcoholic medium containing about 50–70% alcohol based on the alcohol and water present therein.

6. Process according to claim **1**, said contacting being at about 40–60° C., said aqueous alcoholic medium containing about 20–50% alcohol based on the alcohol and water present therein.

7. Process according to claim **1**, wherein the saponification is carried out in about 0.5–4 hours.

8. Process according to claim **1**, said fatty acid containing about 11–22 carbon atoms.

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JOHN D. RANDOLPH, Primary Examiner

U.S. Cl. X.R.

260—45, 398, 656

PO-1050
(5/69)

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,459,776 Dated August 5, 1969

Inventor(s) Szczepanek, et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

1. Col. 1, line 39, "754,854, should be --754,584--.

2. Col. 2, line 9, between "ester" and "alkali" should be inserted --with--.

3. Col. 2, line 47, "2ClaN"should be --2NaCl--.

4. Col. 6, line 8, between "aluminum" and "lead" should be a comma.

5. Col. 7, line 7, "110-118" should be --110-188--.

6. Col. 10, line 24, after "47 g." should be a comma.

7. Col. 10, line 38, "503" should be --50--.

8. Col. 11, line 56, after "obtained" should be a period.

SIGNED AND
SEALED
MAY 5 1970

(SEAL)
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