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1

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OXYGEN CONVERTIBLE POLYMERIC COMPOSITIONS

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This invention relates to novel monomeric and polymeric compositions particularly suited for coating and related applications. More specifically it relates to polymeric compositions which are fusible and/or soluble which, on exposure to oxygen, oxygen containing gases, or other forms of free or liberated oxygen, become converted to insoluble polymers.

The new polymers may be classified as air-drying or air-convertible polymers by an analogy to the natural and synthetic drying and semi-drying oils, the unsaturated fatty acid modified alkyd resins, etc., which are considered as possessing air-drying properties. In the coating and related arts, the terms air-drying or air-convertibility do not refer to the physically dry state which results from the evaporation of a solvent as in a lacquer or from a coating composition such as a varnish, enamel or paint, but to the formation of an insoluble polymer resulting from the reaction of oxygen in the air, with the oils or resins containing a multiplicity of unsaturated groups in their structures.

To be suitable as coating compositions, this air-convertibility should occur at ordinary temperatures such as between 70 and 120° F. although the rate will be much slower at lower temperatures and accelerated at high temperatures. In some cases, it is desirable to accelerate the conversion at temperatures as high as 212° F. or even 260° F. This conversion can be accelerated, at ordinary or at higher temperatures by the addition of catalytic quantities of metal salts, known in the coating arts as driers, such as cobalt, manganese and lead salts, etc., of the fatty acids, linoleic acid, naphthenic acids, resins, etc., as well known and commonly used in this art.

It is, then, an object of this invention, to prepare polymeric compositions which are air-convertible at, at least, ordinary temperatures. It is also another object of this invention to prepare air convertible polymeric compositions in which the convertibility is accelerated by metallic driers.

The objectives of this invention are achieved by the monomers and polymers of this invention in which the monomers have one of the general formulas

$$CH_2{=}C(R){-}Ar{-}Z{-}CH_2R_d$$

and $CH_2{=}C(R){-}Ar{-}Z{-}R_d$, wherein Z and R_d are as defined hereinafter.

Polymers of this invention to be useful as air-drying compositions, i.e., soluble and/or fusible polymers are derived from these monomers to give linear polymers having at least 2 and preferably at least 4 repeating units in the linear chain of the formula,

$$-CH_2-C(R)(Ar-Z-CH_2R_d)- \text{ or } -CH_2-C(R)(Ar-Z-R_d)-$$

Since the primary properties of these polymers are due to the degree of linearity as well as to the length of the backbone polymer chain, it is the purpose of this invention to prepare air-convertible polymers which are substantially linear.

In these monomers and polymers, R represents hydrogen or methyl, and Ar represents an arylene radical.

2

Illustrative examples of the arylene, —Ar—, radical are:

$$-C_6H_4-,\ -C_6H_3(CH_3)-,\ -C_6H_3(C_2H_5)-,\ -C_6H_3(Cl)-,\ -C_6H_3(F)-,\ -C_6H_3(Br)-,\ -C_6H_3(OCH_3)-$$

$$-C_6H_3(OC_6H_5)-,\ -C_6H_3(COOCH_3)-,\ -C_6H_3(COOC_4H_9)-,\ -C_6H_3(N(CH_3)_2)-,\ -C_6H_2(CH_3)_2-$$

$$-C_6H_4-OC_6H_4-,\ -C_6H_4C_6H_4-,\ -C_{10}H_6-,\ -C_{10}H_3(CH_3)-$$

$$-C_6H_4CH{=}CHC_6H_4-,\ -C_6H_4CH_2CH_2C_6H_4-,\ C_6H_4CH_2C_6H_4-,$$

$$-C_6H_4C(CH_3)_2-C_6H_4-, \text{ etc.}$$

As indicated above the arylene radicals can have substituted thereon alkyl, aryl, cycloalkyl, alkoxy, aryloxy, cycloalkoxy, carbalkoxy, halogen, carboxylate and amino derivative groups. The preferred arylene radicals and derivative arylene radicals are those containing 6 to 15 carbon atoms, primarily because of economic factors.

The symbol Z represents functions by which the R_d groups are attached to the arylene nucleus, and thus the R_d group may be attached to

$$CH_2{=}C(R)-Ar-$$

by means of carbon, oxygen and nitrogen bonds individually or in combination of such bonds. Some illustrative examples of the function Z that can be used in the practice of this invention include, but are not limited to the following:

$$-COOCH_2R_d,\ -(CH_2)_nCOOCH_2R_d,\ -COO(CH_2)_nOCH_2R_d$$
$$-(CH_2)_nCOO(CH_2)_{n'}OCH_2R_d,\ -COO(CHRCHRO)_nCH_2R_d$$
$$-CH_2COO(CHRCHRO)_nCH_2R_d,\ -OCH_2R_d$$
$$-O(CH_2)_{n'}OCH_2R_d,\ -O(CHRCHRO)_nCH_2R_d,\ -(CH_2)_nOCH_2R_d$$
$$-(CH_2)_n-O-(CH_2)_{n'}OCH_2R_d,\ -(CH_2)_nO(CHRCHRO)_nCH_2R_d$$
$$-O(CH_2)_nOCOR_d,\ -(CH_2)_nO(CH_2)_{n'}OCOR_d$$
$$-(CH_2)_nO(CHRCHRO)_nCOR_d,\ -(CH_2)_{n'}OCOR_d$$

$$O(CH_2)_{n'}O(CHRCHRO)_nOCR_d,\ -\left(OCHRCHR\right)_nOCOR_d$$

$$-N(R)(CH_2)_nCOOCH_2R_d,\ -N(CHRCOOCH_2R_d)_2$$

$$-N(R)(CH_2)_nCOO(CH_2)_{n'}OCH_2R_d,\ -N(R)(CH_2)_nCOO(CH_2)_{n'}OCOR_d$$

$$-N(R)(CH_2)_nCOO(CHRCHRO)_nOCR_d,\ -OCH_2CH(OCOR'')-CH_2(OCOR_d)$$

$$-OCH_2CH(OCOR_d)CH_2(OCOR''),\ -OCH_2CH(OCH_2R_d)-CH_2(OCOR''),\ -OCH_2CH(OCOR'')CH_2(OCH_2R_d)$$

$$-CH(OCOR'')-CH_2(OCH_2R_d),\ -CH(OCH_2R_d)-CH_2(OCOR''),\ -CH(OCOR'')CH_2(OCOR_d),\ -CH(OCOR_d)CH_2(OCOR'')$$

$$-CH_2R_d,\ -(CH_2)_{n''}CH_2R_d$$

etc., wherein *n* represents a numerical value of 1 to 5, *n'* represents a numerical value of 2 to 12, R represents H or CH_3, and R'' represents a hydrocarbon radical of from 1 to 18 carbon atoms, including R_d radicals, e.g., CH_3 to $C_{18}H_{37}$, C_6H_5, $CH_3C_6H_4$, C_6H_{11}, etc., and R_d represents an unsaturated hydrocarbon radical more fully defined hereinafter.

An examination of the above illustrative examples will confirm that the R_d group is attached to the arylene radical, through ester, ether, amino and hydrocarbon

linkages. This may be further demonstrated by a few specific examples which fall into these classes, thus

Class A esters, e.g.:

$CH_2=CHC_6H_4COOCH_2R_d$
$CH_2=CHC_6H_4CH_2COOCH_2R_d$
$CH_2=CHC_6H_4OCH_2COOCH_2R_d$
$CH_2=CHC_6H_4NHCH_2COOCH_2R_d$
$CH_2=CHC_6H_4CH_2N(CH_2COOCH_2R_d)_2$
$CH_2=C(CH_3)CH_4COOCH_2CH_2OCH_2R_d$, etc.

which are derivatives of alcohols of the formula R_dCH_2OH.

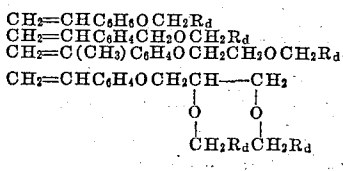
Class B esters, e.g.:

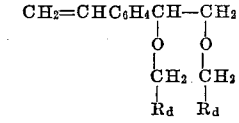
$CH_2=CHC_6H_4CH_2OCOR_d$
$CH_2=C(CH_3)C_6H_4OCH_2CH_2OCOR_d$
$CH_2=CHC_6H_4COOCH_2CH_2OCOR_d$
$CH_2=CHC_6H_4CH_2NHCH_2COOCH_2CH_2OCOR_d$

which are derivatives of acids of the formula R_dCOOH.

Class C esters, e.g.:

$CH_2=CHC_6H_6OCH_2R_d$
$CH_2=CHC_6H_4CH_2OCH_2R_d$
$CH_2=C(CH_3)C_6H_4OCH_2CH_2OCH_2R_d$





which are derivatives of either the alcohols of the formula R_dCH_2OH or their halides, R_dCH_2X.

Class D hydrocarbons, e.g.:

$CH_2=CHC_6H_4CH_2R_d$
$CH_2=CHC_6H_4CH_2CH_2R_d$

which are derivatives of either the alcohol R_dCH_2OH through standard alkylation or derivatives of the halide R_dCH_2X through standard alkylation or Grignard reaction. In the event the hydrocarbon group is attached to the aromatic nucleus by alkylation the group is generally attached through the second carbon atom from the end of the aliphatic chain.

Preferred Z groups are defined in the following tables which illustrate structures of the monomers of this invention:

	Z	
$CH_2=CR-Ar-$	$-COO-$	$-CH_2R_d$
$CH_2=CR-Ar-$	$-COO(CH_2)_nO-$	$-CH_2R_d$
$CH_2=CR-Ar-$	$-COO(CHRCHRO)_n-$	$-CH_2R_d$
$CH_2=CR-Ar-$	$-(CH_2)_nCOO-$	$-CH_2R_d$
$CH_2=CR-Ar-$	$-(CH_2)_nCOO(CH_2)_n'O-$	$-CH_2R_d$
$CH_2=CR-Ar-$	$-(CH_2)_nCOO(CHRCHRO)_n-$	$-CH_2R_d$
$CH_2=CR-Ar-$	$-O-$	$-CH_2R_d$
$CH_2=CR-Ar-$	$-O(CH_2)_n'O-$	$-CH_2R_d$
$CH_2=CR-Ar-$	$-O(CHRCHRO)_n-$	$-CH_2R_d$
$CH_2=CR-Ar-$	$-(CH_2)_nO-$	$-CH_2R_d$
$CH_2=CR-Ar-$	$-(CH_2)_nO(CH_2)_n'O-$	$-CH_2R_d$
$CH_2=CR-Ar-$	$-(CH_2)_nO(CHRCHRO)_n-$	$-CH_2R_d$
$CH_2=CR-Ar-$	$-NR(CH_2)_nCOO-$	$-CH_2R_d$
$CH_2=CR-Ar-$	$-NR(CH_2)_nCOO(CH_2)_n'O-$	$-CH_2R_d$
$CH_2=CR-Ar-$	$-N(CHRCOO-)_2$	$(-CH_2R_d)_2$
$CH_2=CR-Ar-$	$-OCH_2CH(CH_2OC(O)R')-O-$	$-CH_2R_d$
$CH_2=CR-Ar-$	$-OCH_2CH(OC(O)R')CH_2O-$	$-CH_2R_d$
$CH_2=CR-Ar-$	$-CH(OC(O)R')-CH_2O-$	$-CH_2R_d$
$CH_2=CR-Ar-$	$-CH(CH_2OC(O)R')-O-$	$-CH_2R_d$
$CH_2=CR-Ar-$	$-(CH_2)_nOC(O)-$	$-R_d$
$CH_2=CR-Ar-$	$-(CH_2)_nO(CH_2)_n'OC(O)-$	$-R_d$
$CH_2=CR-Ar-$	$-(CH_2)_nO(CHRCHRO)_nC(O)-$	$-R_d$
$CH_2=CR-Ar-$	$-O(CH_2)_n'OC(O)-$	$-R_d$
$CH_2=CR-Ar-$	$-O(CH_2)_n'O(CHRCHRO)C(O)-$	$-R_d$
$CH_2=CR-Ar-$	$-O(CHRCHRO)_nC(O)-$	$-R_d$
$CH_2=CR-Ar-$	$-NR(CH_2)_nCOO(CH_2)_n'OC(O)-$	$-R_d$
$CH_2=CR-Ar-$	$-NR(CH_2)_nCOO(CHRCHRO)_nC(O)-$	$-R_d$
$CH_2=CR-Ar-$	$-(CH_2)_n-$	$-R_d$
$CH_2=CR-Ar-$	$-OCH_2CH(CH_2OC(O)R')-CH_2OC(O)-$	$-R_d$
$CH_2=CR-Ar-$	$-OCH_2CH(OC(O)R')-OC(O)-$	$-R_d$
$CH_2=CR-Ar-$	$-CHCH_2OC(O)-$ (OC(O)R')	$-R_d$
$CH_2=CR-Ar-$	$-CH(OC(O)-)-CH_2OC(O)R'$	$-R_d$
$CH_2=CR-Ar-$	$-CH(CH_3)-$	$-R_d$
$CH_2=CR-Ar-$	$-CH_2-$	$-R_d$

While the above preferred compounds have $-(CH_2)_n$ and —CHRCHRO— groups in which R is hydrogen or methyl, it is also possible to use similar alkylene groups which have a lower alkyl side branch, that is, up to 4 carbon atoms. Moreover, while glyceryl derivatives are shown and are preferred, equivalent groups such as derived from penta-erythritol and other polyhydric alcohols can also be used.

Specific typical compounds illustrative of the monomers of this invention are those of the above formulas in which Ar is the phenylene-group, $-CH_2R_d$ is the linoleyl alcohol radical and Z is:

$-COO-$, $-COOCH_2CH_2O-$, $-COO(CH_2)_3O-$
$-COOCH_2CH_2O-$, $-COO(CH_2CH_2)_2O-$
$-COOCH_2CH(CH_3)O-$, $-(CH_2)_3COO-$, $-CH_2COO-$
$-CH_2COOCH_2CH_2O-$, $-CH_2CH_2COOCH_2CH_2CH_2O-$
$-CH_2COO(CH_2CH_2O)_2-$, $-O-$, $-OCH_2CH_2O-$
$-OCH_2CH_2CH_2O-$, $-OCH_2CH_2O-$, $-O(CH_2CH_2O)_4-$
$-(CH_2)_4O-$, $-CH_2CH_2O-$, $OCH_2CH_2O(CH_2)_8O-$
$-OCH_2CH_2OCH_2CH(CH_3)O-$, $-OCH_2CH_2OCH_2CH_2O-$
$-NH-CH_2COO-$, $-N(CH_3)CH_2COO-$, $-NH-(CH_2)_4COO-$
$-NH-(CH_2)_5COOCH_2CH_2O-$, $-N(CHCOO-)_2$

$-OCH_2CH-O-$, $-OCH_2CH-O-$,
$CH_2OC(O)CH_3$ $CH_2OC(O)C_7H_{15}$

$-OCH_2CHCH_2O-$, $-OCH_2CHCHO-$, $-CH-CH_2O-$
$OC(O)CH_3$ $OC(O)C_{10}H_{21}$ $OC(O)C_3H_7$

$-CH-CH_2O-$, $-CH-O-$, $-CH-O-$, etc.
$OC(O)C_6H_5$ $CH_2OC(O)C_9H_{19}$ $CH_2OC(O)C_6H_{11}$

Other typical monomeric compounds are those in which tolylene, naphthylene, xylylene, diphenylene and chlorophenylene radicals are substituted in the above compounds for the phenylene group. Likewise other typical monomers are those in which the linoleyl alcohol radical is replaced by oleyl, linoleyl, licanyl, eleostearyl, palmitoleyl alcohol radicals, etc.

Other specific typical monomers are those of the above formulas in which Ar is phenylene, R_d is the hydrocarbon portion of linoleic acid and the Z radical is as follows:

$-CH_2OC(O)-$, $CH_2CH_2OC(O)-$, $-(CH_2)_4OC(O)-$
$-CH_2OCH_2CH_2OC(O)-$, $-CH_2O(CH_2CH_2O)_2C(O)-$
$-CH_2OCH_2CH(CH_3)OC(O)-$, $-OCH_2CH_2OC(O)-$
$-O(CH_2)_5OC(O)-$, $-OCH_2CH_2OCH_2CH_2OC(O)-$
$-O(CH_2)_4OCH_2CH_2OC(O)-$, $-OCH_2CH(CH_3)OC(O)-$
$-NHCH_2COOCH_2CH_2OC(O)-$
$-N(CH_3)CH_2COOCH_2CH_2OC(O)-$, $-CH_2CH_2-$, $-(CH_2)_5-$

$-OCH_2CH-CH_2OC(O)-$, $-OCH_2CH-CH_2OC(O)-$
$OC(O)CH_3$ $OC(O)C_7H_{15}$

$-OCH_2CH-OC(O)-$, $-OCH_2CH-OC(O)-$
$CH_2OC(O)CH_3$ $CH_2OC(O)C_{10}H_{21}$

$-CHCH_2OC(O)-$, $-CHCH_2OC(O)-$, $-CH-OC(O)-$
$OC(O)C_6H_5$ $OC(O)C_6H_{11}$ $CH_2OC(O)CH_3$

$-CH-OC(O)-$, etc.
$CH_2OC(O)C_9H_{19}$

The monomers of this invention are readily prepared through classical organic reactions when based on alcohols, acids, and halides of the formulas R_dCH_2OH, R_dCOOH, and R_dCH_2X respectively, as illustrated by the following examples. The Class A esters are readily prepared by reacting an R_dCH_2OH alcohol with an appropriate vinyl aryl carboxy compound as illustrated by vinyl benzoic acid compounds, e.g.,

$$CH_2=CHC_6H_4COOR'_i+R_dCH_2OH\rightarrow CH_2=CHC_6H_4COOCH_2R_d+R'OH$$

wherein R' is hydrogen or a hydrocarbon radical containing one to twelve carbon atoms. In this reaction the preferred groups for R' are hydrogen and the lower alkyl radicals containing one to four carbon atoms, e.g., H, CH_3, C_2H_5, C_3H_7, and C_4H_9.

Another convenient method of preparing these esters is to react the acid chlorides with the alcohols in the presence of a hydrohalide acceptor (HAC) such as triethyl amine, tributyl amine, pyridine, Na_2CO_3, etc., according to the reaction, e.g.,

$$CH_2=CHC_6H_4COCl + R_dCH_2OH \xrightarrow{HAC} CH_2=CHC_6H_4COOCH_2R_d$$

Alternately, the acid anhydrides may be used, thus,

$$(CH_2=CHC_6H_4CO)_2O+R_dCH_2OH\rightarrow CH_2=CHC_6H-COOCH_2R_d+CH_2=CHC_6H_4COOH$$

While the vinyl benzoyl derivative is used to illustrate the ester formation, it is used only to typify the other acids falling within the scope of this invention, and the acids, alkyl esters and acid chlorides of the other acids

are also used, for example, $CH_2=CHC_6H_4CH_2COOH$ (from $CH_2=CHC_6H_4CH_2Cl$ with NaCN and H_2O); $CH_2=CHC_6H_4OCH_2COOH$ (from $CH_2=CHC_6H_4ONa$ and $ClCH_2COOH$); $CH_2=CHC_6H_4NHCH_2COOH$ (from $CH_2=CHC_6H_4CH_2Cl+HN(CH_2COONa)$, etc. Typical examples of R_dCH_2OH alcohols used in the esterification are

(a) 9,12 linoleyl alcohol,
$CH_3(CH_2)_3(H_2CH=CH)_2(CH_2)_7CH_2OH$

(b) Linolenyl alcohol,
$CH_3(CH_2CH=CH)_3(CH_2)_7CH_2OH$,

(c) Arachidonyl alcohol,
$CH_3(CH_2)_3(CH_2CH=CH)_4(CH_2)_3CH_2OH$,

(d) Licanyl alcohol, $CH_3(CH_2)_3(CH=CH)_2(CH_2)_4CO(CH_2)_2CH_2OH$,

(e) Parinaryl alcohol,
$CH_3CH_2(CH=CH)_4(CH_2)_7CH_2OH$,

(f) Eleostearyl alcohol,
$CH_3(CH_2)_3(CH=CH)_3(CH_2)_7CH_2OH$,

(g) 9,11 linoleyl alcohol,
$CH_3(CH_2)_5(CH=CH)_2(CH_2)_7CH_2OH$.

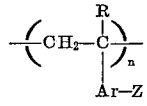
These alcohols are obtained by catalytic reduction with hydrogen, or by chemical reduction methods as by the Beauvault Blanc reaction of an alcohol such as butyl alcohol with sodium, or by lithium hydride, etc., of the corresponding fatty acids, or their natural or synthetic esters, all of which can be represented by the reduction of methyl or glyceryl linoleate, whereby the linoleic acid moiety is reduced to the corresponding alcohol, thus

$$CH_3(CH_2)_3(CH_2CH=CH)_2(CH_2)_7COOCH_3 \xrightarrow{[H]} CH_3(CH_2)_3(CH_2CH=CH)_2(CH_2)_7CH_2OH,$$

and

$$\begin{array}{l} C_{17}H_{31}COOCH_2 \\ C_{17}H_{31}COOCH \\ C_{17}H_{31}COOCH_2 \end{array} \xrightarrow{[H]} \begin{array}{l} CH_2OH \\ CHOH \\ CH_2OH \end{array} + 3C_{17}H_{31}CH_2OH.$$

It will be observed that the seven alcohols (a) to (g) listed above contain at least two —CH=CH— unsaturated structures; in the first three, (a) to (c), the double bonds are not conjugated whereas in (d) to (g), the double bonds are conjugated. By subjecting esters of the type used in this invention to a directed polymerization, fully described hereinafter, they are polymerized to linear form,



with the Ar—Z group pendant to the polymer backbone. In this class of polymers, it is observed that when the R_d group contains conjugated unsaturation, more rapid air-drying is achieved than when the double bonds are not conjugated.

For very rapid drying, those polymers in which at least some of the R_d groups contain conjugated unsaturation are preferred. When very fast or very rapid drying rates are not required in the coating composition, practical and satisfactory compositions can be prepared from the monomers in which R_d contain only one —CH=CH— group. Illustrative of such alcohols containing only one —CH=CH— group from which the esters are prepared are

Palmitoleyl alcohol,
$(CH_3)(CH_2)_5CH=CH(CH_2)_7CH_2OH$,
Oleyl alcohol, $CH_3(CH_2)_7CH=CH(CH_2)_7CH_2OH$,
Petroselinyl alcohol,
$CH_3(CH_2)_{10}CH=CH(CH_2)_4CH_2OH$,
Vaccenyl alcohol, $CH_3(CH_2)_5CH=CH(CH_2)_9CH_2OH$,
Gadoleyl alcohol, $CH_3(CH_2)_9CH=CH(CH_2)_7CH_2OH$,
Cetoleyl alcohol, $CH_3(CH_2)_9CH=CH(CH_2)_9CH_2OH$,
Erucyl alcohol, $CH_3(CH_2)_7CH=CH(CH_2)_{11}CH_2OH$,
Nervonyl alcohol, $CH_3(CH_2)_7CH=CH(CH_2)_{13}CH_2OH$,

all of which are obtainable by reduction of the corresponding acids or esters.

It is readily observable that in these monoolefinic and polyolefinic alcohols that (1) there is no terminal $CH_2{=}C<$ structure, rather the terminal group is a CH_3- group, (2) the first double bond in the structure is removed from the oxygen atom of the alcohol (and therefore in its esters) by at least 4 carbon atoms and by as many as 14 carbon atoms, and therefore are not activated by the ester structure, (3) the first double bonds are removed by at least 1 carbon atom from the terminal $-CH_3$ group which is not an activating group, and (4) there may be 1 to 4 $-CH{=}CH-$ groups in the unsaturated portion of the alcohol molecule. In these respects the polymers of the aryl esters of these alcohols are similar in character to the structures of drying oil and are in contrast to polymers of the allyl and methallyl acrylic esters which do not air dry. The radical R_d of the R_dCH_2OH alcohols used in the preparation of these esters may be described as an unsaturated fatty or aliphatic hydrocarbon containing 15 to 23 carbon atoms, a terminal $-CH_3$ group, 1 to 4 $-CH{=}CH-$ groups and the remainder being $-CH_2-$ groups. In some cases, one $-CH_2-$ group may be replaced, as in the case of licanyl alcohol, by a keto,

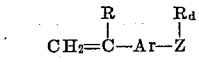
group. These alcohols and their simple non-monomeric esters, such as the benzoates or tertiary butyl benzoates, do not air-dry, whereas the polymers of this invention, air-dry readily.

For the purposes of this invention the esters of pure individual alcohols are not required, although some of them have become available commercially in different degrees of purity. Mixtures of the alcohols, such as are obtained by the reduction of vegetable, animal and marine oils and fats are satisfactory. Since such oils and fats are mixtures of various glycerides, the alcohols resulting from the reduction of ester groups correspond equivalently to the amounts of acid moiety present in the glyceride. Table 1 gives the percentage composition of the fatty acids in a number of drying oils, which on reduction produce an equivalent amount of the corresponding alcohols.

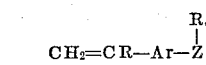
TABLE 1

Oil	Percent of Total Fatty Acid						
	Palmitic	Stearic	Oleic	Linoleic	Linolenic	Licanic	Eleostearic
Soybean	6.5	4.2	33.6	52.6	2.3	--------	--------
Oiticica	5.0	5.0	5.9	10.0	--------	74.1	--------
Tung	4.0	1.5	15.0	--------	--------	--------	79.5
Linseed	5.0	3.5	5.0	61.5	25.0	--------	--------
Perilla	7.5	--------	8.0	38.0	46.5	--------	--------

It will be noted in Table 1 that all of the oils have measurable amounts of compounds having one or more than one double bond in the fatty acid and therefore, the derived alcohols, since only the ester group is reduced, have a substantial amount of suitable mono- and polyunsaturation suitable for the purposes of this invention. The alcohols derived from palmitic and stearic acids are saturated alcohols, and if present in the mixture during esterification also become converted to esters similar in structure to those of the

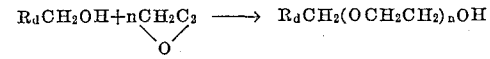


type and copolymerize with the

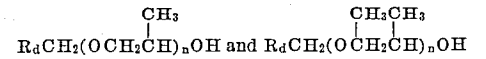


monomers, lending flexibility and ductility to the polymerization product. Mixture of such alcohols are useful and the monomers resulting from such mixtures are also contemplated in the practice of the invention.

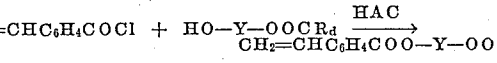
Instead of the alcohols R_dCH_2OH, certain derivatives of the alcohols, such as the alkylene oxide addition products can be used, and they are readily prepared by reacting the oxide with the alcohols in the presence of alkali, thus



wherein n is one to five, and if desired, may be increased, for certain application, to as high as 9 or 10. Propylene oxide and butene-2 oxide produce the corresponding alcohols,



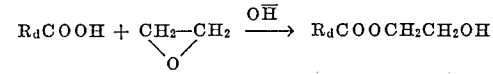
Another class of alcoholic derivatives which can be used with the vinyl aryl carboxy compounds have the general formula, $R_dCOO-Y-OH$ as illustrated by the reaction with vinyl benzoyl chloride,



Typical examples of the $R_dCOO-Y-OH$ alcohols are β-hydroxyethyl linoleate, β-hydroxyethyl oleate and β-hydroxyethyl linolenate which can be represented by $R_dCOOCH_2CH_2OH$. These hydroxy alkyl ester intermediates are prepared by esterification of the R_dCOOH acids with glycols, e.g., ethylene glycol, thus

$$R_dCOOH + HOCH_2CH_2OH \rightarrow R_dCOOCH_2CH_2OH$$

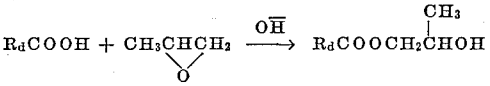
or by the reaction of the acid with ethylene oxide in the presence of a base, thus



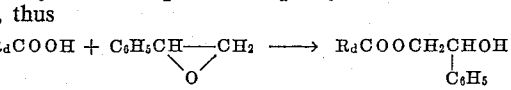
When an excess of oxide is used for example, x' moles, when x' equals 1 to 5, then the polyoxyalkylene alcohol is obtained, e.g.,



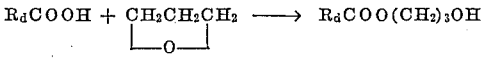
With propylene oxide, the corresponding ester is obtained,



while styrene oxide produces a phenyl substituted derivative, thus



With trimethylene oxide or trimethylene glycol, the hydroxypropyl esters are obtained, as



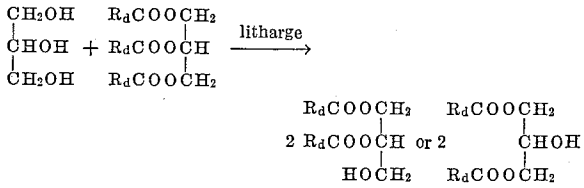
Thus, it may be seen that when —Y— represents a radical of a dihydric alcohol, the intermediate

$$R_dCOO-Y-OH$$

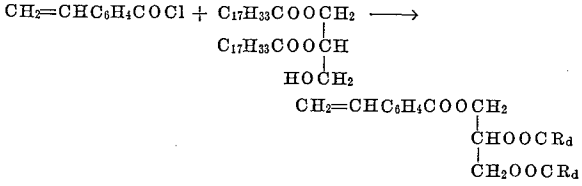
is readily prepared by esterification of only one of the hydroxy groups of the diol with an R_dCOOH acid, and if the cyclic oxide corresponding to the diol is known or available, it may be used instead of the diols. The radical —Y— may also represent the radical derived from alcohols higher than the diols, such as the triols, tetrols, pentols, etc., in which case more lightly substituted derivatives falling within the general formula of the intermediates, $R_dCOO-Y-OH$ compounds are obtained.

Illustrative examples of some of the many triol, tetrol, etc. derivatives are glyceryl dioleate, glyceryl dilinoleate, glyceryl dilinolenate, pentaerythritol trioleate, etc. The

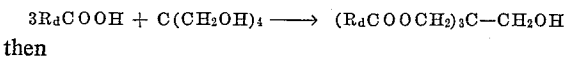
glyceryl derivatives are readily prepared, as is known in the alkyd resin and coating arts, by transesterification of oils with glycerine, thus



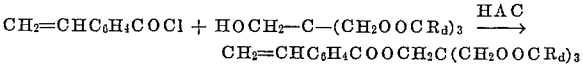
which, as indicated hereinabove, are easily converted to the desired ester as is illustrated by the reaction of vinyl benzoyl chloride and glyceryl dioleate:



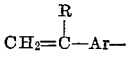
When —Y— is derived from a trihydric, tetrahydric, or higher alcohol, all but one of the alcoholic hydroxy groups may be esterified by the R_dCOOH acid and the residual hydroxyl group converted to an ester as shown with the glyceryl dioleate hereinabove and illustrated also by pentaerythritol, thus,



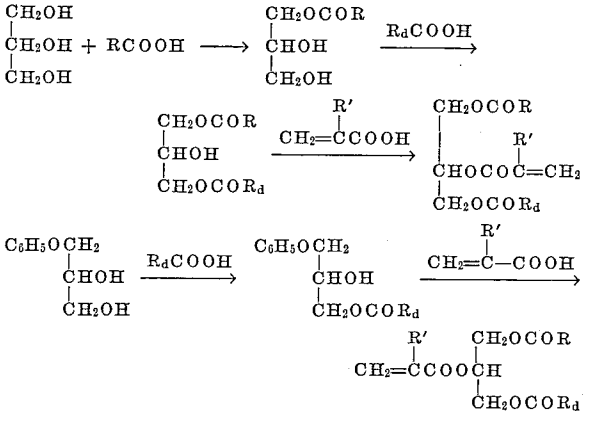
then



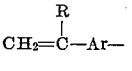
However, in the practice of this invention, the monomer contains only *one*



group and at least one R_dCOO— group, as illustrated with the glycols, glycerine and pentaerythritol. However, when only one of the hydroxyls in polyhydric alcohols containing more than the two —OH groups is converted to an R_dCOO— ester, the remaining —OH groups can be converted to groups other than R_dCOO groups, such as ordinary ester groups, R″COO— or ether groups, R″O—, wherein R″ is a hydrocarbon containing 1 to 18 carbon atoms, as for example,

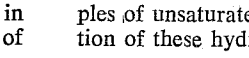


Accordingly, these esters can also be defined as esters of polyhydric alcohols possessing two to five hydroxyl groups, said esters containing only one



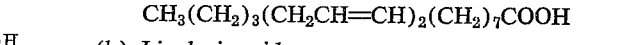
group, and at least one R_dCOO— group. Typical exam-

ples of unsaturated R_dCOOH acids useful in the preparation of these hydroxyalkyl esters intermediates,

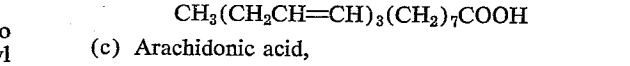


and from which the R_dCOO— group is derived, are

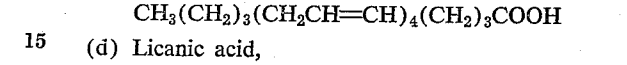
(a) 9, 12 linoleic acid,



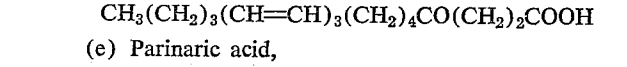
(b) Linolenic acid,



(c) Arachidonic acid,



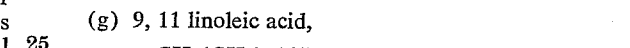
(d) Licanic acid,



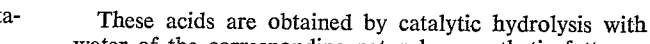
(e) Parinaric acid,



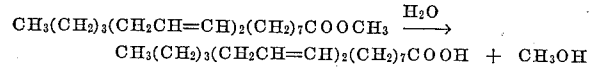
(f) Eleostearic acid,



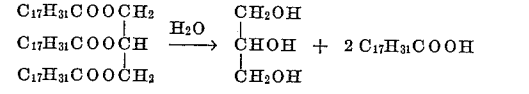
(g) 9, 11 linoleic acid,



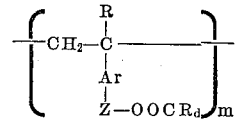
These acids are obtained by catalytic hydrolysis with water of the corresponding natural or synthetic fatty esters, all of which can be represented by the hydrolysis of methyl or glyceryl linoleate, thus



and



It will be observed that the seven acids (a) to (g) listed above contain at least two —CH=CH— unsaturated structures; in the first three (a) to (c), the double bonds are not conjugated whereas in (d) to (g), the double bonds are conjugated. As observed in the polymers derived from R_dCH_2OH alcohol polymers having the formula



and which contain an R_dCOO— linkage on the Z group, more rapid drying is achieved when the unsaturation in the R_d group is conjugated than when it is non-conjugated. Accordingly, for very rapid drying, those polymers in which at least some of the R_dCOO— groups contain conjugated unsaturation are preferred.

When very fast or very rapid drying rates are not required in the coating composition, practical and satisfactory compositions can be prepared from the monomers in which R_dCOO contain only one —CH=CH— group. Illustrative of such fatty acids containing only one —CH=CH— group from which the esters are prepared are

Palmitoleic acid, $(CH_3)(CH_2)_5CH{=}CH(CH_2)_7COOH$,
Oleic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$,
Petroselinic acid, $CH_3(CH_2)_{10}CH{=}CH(CH_2)_4COOH$,
Vaccenic acid, $CH_3(CH_2)_5CH{=}CH(CH_2)_9COOH$,
Gadoleic acid, $CH_3(CH_2)_9CH{=}CH(CH_2)_7COOH$,
Cetoleic acid, $CH_3(H_2)_9CH{=}CH(CH_2)_9COOH$,
Erucic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$,
Nervonic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_{13}COOH$,

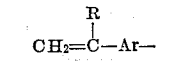
all of which are obtainable by the hydrolysis of the corresponding natural esters.

It is readily observable that in these monoolefinic and polyolefinic R_dCOO— groups that (1) there is no terminal $CH_2{=}C<$ structure, rather the terminal group is a CH_3— group, (2) the first double bond in the structure is removed from the oxygen atom of its esters, by at least 4 carbon atoms and by as many as 14 carbon atoms, and therefore are not activated by the ester structure, (3) the first double bonds are removed by at least 1 carbon atom from the terminal —CH_3 group which is not an activating group, and there are 1 to 4 —CH=CH— groups in the unsaturated portion of the acid molecule. In this regard they are similar to the R_dCH_2OH alcohol, and the R_d portion of both the R_dCH_2OH and R_dCOOH are identically defined.

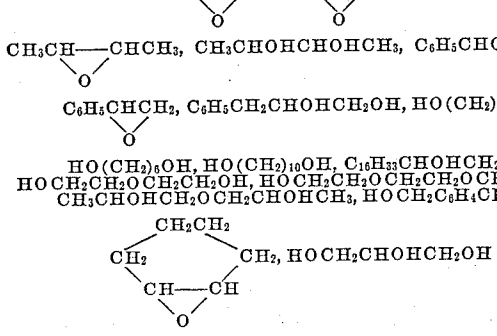
For the purposes of this invention the pure individual R_dCOOH acids are not required although some of them have become available commercially in different degrees of purity. Mixtures of the acids, such as are obtained by the hydrolysis of vegetable, animal and marine oils and fats are satisfactory. Since such oils and fats are mixtures of various glycerides, the acids resulting from the hydrolysis of the ester groups correspond equivalently to the amounts of acid moiety present in the glyceride. Table 1 gives the percentage composition of the fatty acids in a number of drying oils, which on hydrolysis produce an equivalent amount of the corresponditng acids and are useful in preparing the monomers suitable for the practice of this invention.

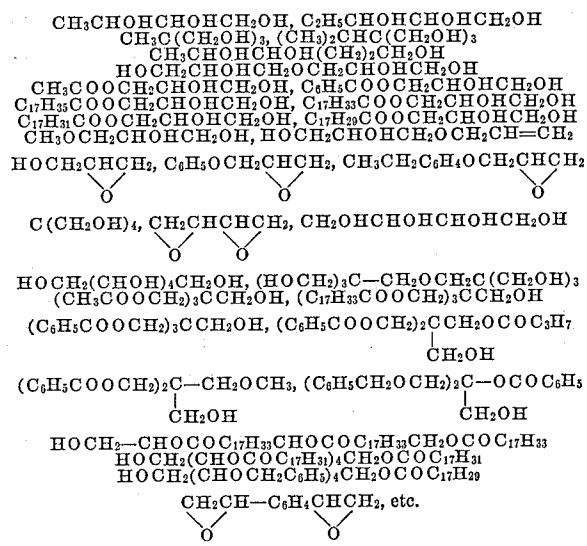
It will be noted in Table 1 that all of the oils have measurable amounts of compounds having one or more than one double bond in the fatty acid and therefore, the derived acids have a substantial amount of suitable mono- and poly-unsaturation suitable for the purposes of this invention. Palmitic and stearic acids are saturated acids, and if present in the mixture during esterification with a polyhydric alcohol, HO—Y—OH, also become converted to esters and copolymerize with the other monomers, lending flexibility and ductility to the polymerization product. Mixture of such acids are useful and the monomeric esters resulting from such mixtures are also contemplated in the practice of the invention.

As shown hereinabove, the radical, —Y—, is derived from polyols containing at least two hydroxyl groups, one hydroxyl group of which is used for bonding to the

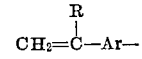


moiety and at least one to the R_dCOO-moiety, so that the radical, —Y—derived from the polyol may be written as —Y—$(OOCR_d)_p$, wherein *p* represents an integer of one to five, and —Y— is a polyvalent radical containing 2 to 18 carbon atoms in which all the valencies not occupied by the one bond to $CH_2{=}C(Ar)$—and R_dCOO— bonds are occupied by R", OR", OCOR", and —OH radicals. Illustrative polyols of the formula HO—Y—OH, as well as some cyclic oxides from which the —Y— groups are derived are,





The Class B esters are readily prepared by reacting an R_dCOOH acid compound with the suitable alcohol derivative of the



radicals as illustrated with vinylbenzyl alcohol,

$$CH_2{=}CHC_6H_4CH_2OH + R_dCOOR' \rightarrow CH_2{=}CHC_6H_4CH_2OCOR_d$$

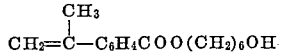
An alternate method is to use the acid chloride in the presence of a hydrohalide acceptor,

$$R_dCOCl + HOCH_2C_6H_4CH{=}CH_2 \xrightarrow{HAC} R_dCOOCH_2C_6H_4CH{=}CH_2$$

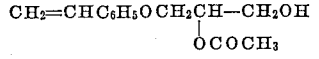
The vinyl benzyl alcohol is illustrative of other alcohols which can be used, e.g.,

$CH_2{=}CHC_6H_4O(CH_2CH_2O)_nH$
(from vinyl phenol and ethylene oxide)

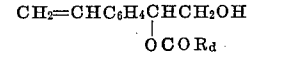
$CH_2{=}CHC_6H_4CO(OCH_2CH_2)_nOH$
(from vinyl benzoic acid and ethylene oxide)



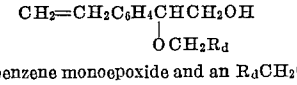
(from isopropenyl benzoic acid and hexamethylene glycol)



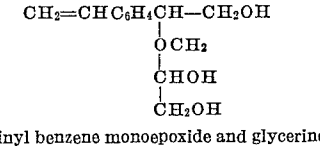
(from vinylphenyl glycidyl ether and acetic acid)



(from divinyl benzene monoepoxide and an R_dCOOH acid)

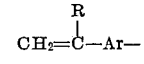


(from divinyl benzene monoepoxide and an R_dCH_2OH alcohol)



(from divinyl benzene monoepoxide and glycerine), etc.

The Class C ethers are also readily prepared by reacting an R_dCH_2OH alcohol or a R_dCH_2X halide with a suitable halide or alcohol derivative of a



radical. These reactions may be illustrated in one case with vinyl benzyl chloride, thus

$$CH_2{=}CHC_6H_4CH_2Cl + R_dCH_2ONa \rightarrow NaCl + CH_2{=}CHC_6H_4CH_2OCH_2R_d$$

$$CH_2{=}CHC_6H_4CH_2Cl + R_dCH_2(OCH_2CH_2)_nONa \rightarrow NaCl + CH_2{=}CHC_6H_4CH_2O(CH_2CH_2O)_nCH_2R_d$$

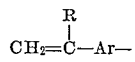
Instead of vinyl benzyl chloride, other halides such as

$CH_2=CHC_6H_4OCH_2CH_2Cl$
(from $CH_2=CHC_6H_4ONa + ClCH_2CH_2Cl$)

$CH_2=C(CH_3)C_6H_4OCH_2CH_2OCH_2CH_2Cl$

(from $CH_2=C(CH_3)C_6H_4ONa + ClCH_2CH_2OCH_2CH_2Cl$)
$CH_2=CHC_6H_4COOCH_2CH_2Cl$
(from $CH_2=CHC_6H_4COOH$ and $HOCH_2CH_2Cl$)

etc. may be used. The inverse reaction may also be used where the alcohol function is attached to the



radical, thus

$$CH_2=CHC_6H_4CH_2ONa+R_dCH_2X \rightarrow CH_2=CHC_6H_4CH_2OCH_2R_d$$
$$CH_2=CHC_6H_4OCH_2CH_2ONa+R_dCH_2X \rightarrow CH_2=CHC_6H_4OCH_2CH_2OCH_2R_d$$

in which the alcoholates are prepared from the alcohol and an alkali metal. Other alcohols which can be used as alcoholates with R_dCH_2X are,

$CH_2=C(CH_3)-C_6H_4(OCH_2CH_2)_nOH$

$CH_2=CH-C_6H_4CO(OCH_2CH_2)_nOH$

$CH_2=CHC_6H_4CH_2(OCH_2CH_2)_nOH$, etc.

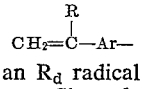
The Class D hydrocarbons are best prepared through the Grignard reaction, thus,

$$CH_2=CHC_6H_4CH_2Cl + R_dCH_2MgX \longrightarrow CH_2=CHC_6H_4CH_2CH_2R_d$$
$$CH_2=CHC_6H_4Br + R_dCH_2MgX \longrightarrow CH_2=CHC_6H_4CH_2R_d$$

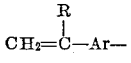
or

$$CH_2=CHC_6H_4CH_2X + R_dCH_2X \xrightarrow{2Na} CH_2=CHC_6H_4CH_2CH_2R_d + 2NaX$$

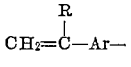
Thus it may be seen that a wide variety of monomers useful in the practice of this invention can be prepared by well-known and established reactions, and that the monomers can be defined as having the general structure



to which is attached an R_d radical through ether, esters or hydrocarbon linkages. Since these monomers contain one



group and at least one R_d— group, they possess a multiplicity of polymerizable double bonds, of which the bond in the



group is very reactive, and at least one other

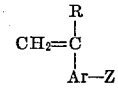
—HC=CH—

group in some cases four —CH=CH— groups.

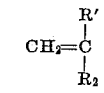
Since in a polymerization, all of the ethylenic groups can participate, it would be expected that crosslinked, insoluble, infusible polymers are obtained from these monomers, and therefore a directed polymerization would be necessary to prepare soluble, fusible polymers and copolymers. When these monomers are polymerized by radical initiation, crosslinked gelled polymers result; and similar insoluble products are obtained with thermal polymerizations. When cationic initiators such as BF_3, $AlCl_3$, H_2SO_4, $SnCl_4$, $TiCl_4$ etc. are used, insoluble, infusible products are likewise obtained.

However, I have discovered that useful linear, soluble polymers and copolymers are obtained when a base-

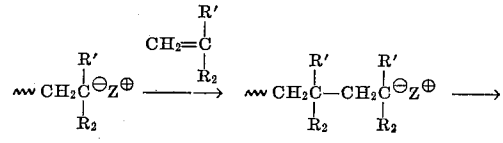
catalyzed polymerization is performed, such as in an anionic polymerization. By an anionic polymerization is meant a polymerization in which the propagation of the polymer chain occurs through a carbanion. This may be illustrated by rewriting the monomers,



as

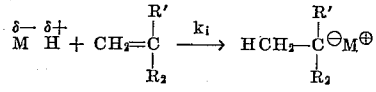


wherein R_2 represents —Ar—Z, thus

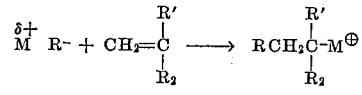


etc, in which $Z^{\oplus}$ is a positive counter ion, usually a metal, typically an alkali or alkaline earth metal. The propagation step is preceded by an initiating step; and initiation may be brought about in a number of ways.

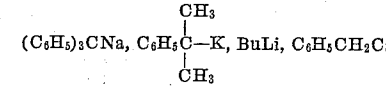
The anionic polymerization can be initiated by an alkali metal hydride such as NaH, LiH, KH, CsH, including various complexes thereof, such as $LiAlH_4$ etc. Designating such hydrides as MH, then the initiating step is



When an alkali metal alkyl is used, the initiating step is given as

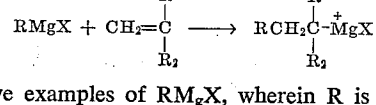


in which the cation $M^{\delta+}$ represents Li, Na, K, Cs etc. and the anion R^- represents methyl, ethyl, propyl, isopropyl, butyl, amyl, isoamyl, benzyl, triphenyl, methyl, phenyl, naphthyl, octyl, etc., preferably containing no more than 12 carbon atoms in said anion. A few typical examples of MR are



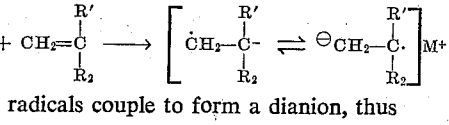
allyl sodium, etc.

A Grignard reagent RM_gX can also be used to initiate an anionic polymerization, thus

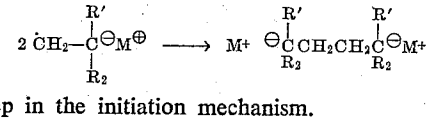


Illustrative examples of RM_gX, wherein R is as defined above, and X is a halogen such as phenyl magnesium bromide, butyl magnesium bromide and chloride, vinyl magnesium bromide, allyl magnesium bromide, etc.

The free alkali metals can also be used to initiate polymerization, especially when the metal, M°, gives up an electron to form an ion radical of the monomer, thus

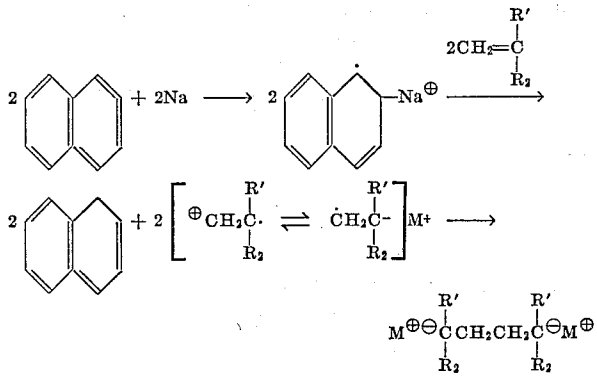


The ion radicals couple to form a dianion, thus

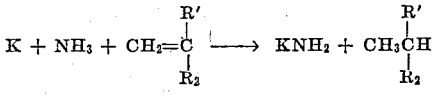


as a step in the initiation mechanism.

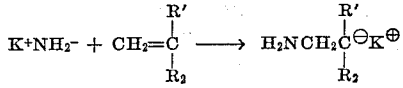
A similar mechanism occurs in the anionic initiation using an alkali metal and naphthalene, anthracene, α-methyl styrene tetramer, etc., as illustrated by naphthalene, thus



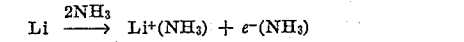
The alkali metals in liquid ammonia are also effective anionic polymerization initiators which may function in either of two ways, e.g., in the case of potassium, calcium, or sodium in liquid ammonia the resulting amide functions as the initiator, thus



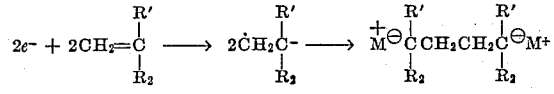
then



In the case of lithium an ion radical is formed in the reaction which acts as the initiator, thus



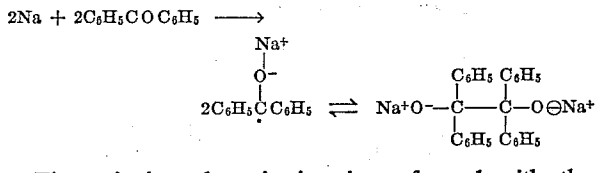
where e^- is an electron, thus



In the ammonia amide series, the order of reactivity of the cations is given as

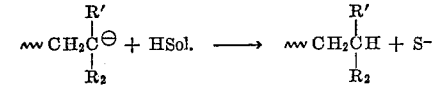
$$KNH_2 > NaNH_2 > LiNH_2 > Ca(NH_2)_2 > Sr(NH_2)_2 > Ba(NH_2)_2$$

In a similar way anionic initiation may be brought about by ketyls which are the reaction products of an alkali or alkaline earth metal with a ketone such as benzophenone in ether, thus

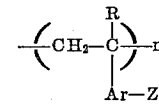


The anionic polymerization is performed with the monomers of this invention, alone or in the presence of a liquid diluent, at temperatures ranging from about —80° C. to 80° C. For most monomers the range of —40° C. to 60° is satisfactory, but in general, —20°C. to 40° C. is more practical.

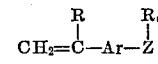
The solvents, or diluents, when used, may be selected from the class of aliphatic and aromatic hydrocarbons, ketones, ethers and esters, such as butane, propane, hexane, heptane, octane, benzene, toluene, xylene, dimethyl, ether, diethyl ether, dibutyl ether, tetrahydrofurane, dioxane, diphenyl ether, dibenzyl ether, dimethyl ethylene glycol ether, dibutyl ethylene glycol ether, diethyl-diethylene glycol ether, etc. The diluent or solvent can also act to control the molecular weight of the polymerization by solvalitic chain transfer with the anion when protonic solvents are used, thus



Anionic polymerizations are also referred to as base-catalyzed polymerizations. For economical use as coating compositions, it is wasteful as well as unnecessary to use homopolymers of the monomers of this invention, since the high activity of polymers having such an abundance of air-drying functions such as in



is not needed in most cases, although they can be used as such in castings for encapsulation or impregnation. In most applications, copolymers with other monomers are preferred, particularly after it was discovered that the air-drying property of these monomers is conferred on the copolymers, which may be dipolymers, tripolymers, etc., depending on the number of additional monomers used as well as on the identity of the



monomer. A typical case is where the monomer is prepared from R_dCOOH acids or R_dCH_2OH alcohols derived from natural oils such as linseed or oiticica oil which contains 5 different compounds, as shown in Table 1.

In many cases, especially with the pure monomers derived from pure alcohols or acids, in which R_d contains four —HC=CH— group, copolymers containing 0.5 to 1% of these monomers are useful, but to achieve better air drying rates, copolymers containing at least 5% are preferable. When the R_d group contains fewer —CH=CH— groups, 10 to 20% of the monomer in the copolymer is advantageous. When the monomer is produced from alcohols or acids having a high percentage of saturated higher fatty acids or alcohols, then 50–80% or more are preferable. Accordingly, depending on the end product desired and the use to which it is to be put, copolymers containing as little as 0.5% are useful. When less than 0.5%, such as 0.1% is used, then drying is greatly reduced, but, in this case, a noticeable plasticizer effect is evident and in this aspect these copolymers are useful and valuable. Obviously, those copolymers having more than 0.1% show higher internal plasticization, and when this particular property is desired, it is achieved by the practice of this invention. Accordingly, a wide range of compositions can be made by copolymerizing these monomers with one or more other monomers containing a vinyl, CH_2=CH— group, a vinylidene CH_2=C< group, or a vinylene —CH=CH— group.

Illustrative examples of other monomers containing such groups are the acrylic esters such as methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, hexyl acrylate, phenyl acrylate, benzyl acrylate, methyl-α-chloroacrylate, etc.; the methacrylic esters such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, methallyl methacrylate, etc.; the vinyl esters such as vinyl chloride, vinyl acetate, vinyl stearate, vinyl benzoate, vinyl methyl phthalate, vinyl ethyl succinate, etc.; the polymerizable amides and nitriles such as N-dimethyl acrylamide, N-diethyl methacrylamide, acrylonitrile, methacrylonitrile, etc.; the alkenyl aryl compounds such as styrene, o-methyl styrene, p-methyl styrene, α-methyl styrene, the chlorostyrene, vinyl methoxy benzene, diallyl benzene, etc.; the vinylidene compounds such as vinylidene cyanide, methylene malonic esters, etc.; vinylene compounds such as vinylene carbonates, and the maleic esters, especially the maleic diesters of the lower alcohols;

the itaconic compounds such as itaconic anhydride, the itaconic esters of the lower and higher aliphatic alcohols; the dienes such as butadiene, isoprene, and the like.

The proportion of the new monomers in copolymers with other monomers will depend, in accordance with the accepted principles of copolymerization, on the reactivity and selectivity constants of the comonomers used in preparing the copolymer, the ratio of the monomers used and the extent of conversion. However, by selecting appropriate conditions for the copolymerization copolymers using the new monomers of this invention, can be made to contain effective and small amounts of these new monomers, for example, of the order of from 0.1% to 0.5% to very high amounts of the order of 99.5% to 99.9% in the final copolymer products.

In anionic copolymerizations, the copolymerization parameter, r_1 and r_2, are sometimes influenced by the solvent is one is used, for example, when a 50% benzene solution of a mixture of 90% vinylacetate and 10% of $CH_2{=}CHC_6H_4COOC_{17}H_{33}$ with Na as an initiator, is polymerized at 30° C., less than 2% of the benzoate feed is found in the copolymer, whereas when the polymerization is performed in bulk without a solvent, about 27% of the benzoate is found in the copolymer. On the other hand, when the benzoate is copolymerized with ethyl acrylate or styrene, 100% of the monomer is found in the copolymer whether the copolymerization is performed in bulk or in a solution. Thus, while it is seen that same monomers polymerize less readily with the monomers of this invention, the resulting copolymers may still be used as air convertible compositions. The comonomers give corresponding repeating units such as

$$-CH_2CH-$$
$$\quad\quad|$$
$$\quad C_6H_5$$

from styrene,

$$-CH_2CH-$$
$$\quad\quad|$$
$$\quad COOCH_3$$

from methyl acrylates, etc.

The polymers and copolymers of this invention may be used as prepared or blended or compounded with other polymers and ingredients. When prepared and obtained in a viscous liquid form they may be used without solvent for casting, laminating and impregnating uses, or, to lower the resin content, or to control or regulate the viscosity, they may be diluted with solvents, or emulsified with water and used in the latex form. When obtained as soft resins, they can be diluted or emulsified, or used as melts to coat or impregnate substrates. When prepared as hard polymers they can be used in solution, or in emulsion, or in dispersions, or as dip-melts, or spray-melts, or fluidized-melts, etc. The polymers and copolymers can be blended with other drying and semi-drying or non-drying oils with or without a solvent; or they can, in a similar way, be blended or reacted with alkyd resin modified with drying or demi-drying oil acids, oil soluble phenolic resin, oil modified phenolic resins, etc. They can be used as blends with other film forming polymers, such as nitro-cellulose, polyvinyl acetate, polymethyl methacrylate, polyvinyl chloride and its copolymers, polystyrene and its copolymers, especially the butadiene copolymers; the blends being achieved either in solution or in emulsion, or without solvents. The polymers and copolymers of this invention, including blends with other polymers, can be converted to varnishes, paints, enamels and impregnants in the usual way and can be mixed with dyes, solvents, pigments, lubricants, stabilizers, etc; as is common in the coating arts. As such, they are useful not only as direct coatings but are particularly satisfactory for the preparation of oil cloths, electrical oil-cloth-insulating tapes, rain coats, linoleums, inks, etc.; when fabrics, paper, cloth, cork, mica, etc. are coated or impregnated with these compositions.

When properly prepared the polymers and copolymers of this invention are substantially colorless or nearly so if the monomer is colorless, and the dried films have excellent resistance to yellowing compared to films prepared from drying oils or drying oil-modified alkyd resins and similar compositions. Also, those polymers in which the R_d group is bonded to the

$$\quad\quad R$$
$$\quad\quad|$$
$$CH_2{=}C-Ar-$$

radical through ether or hydrocarbon linkages, are extremely resistant to acids and alkali which readily hydrolyze alkyd-type resins.

The following examples illustrate the practice of this invention and are used by way of illustration and not intended in any way to limit the scope of this invention nor the manner in which it can be practiced. All parts and percentages are parts and percentages by weight, unless otherwise specified.

Example I

Two hundred sixty-six parts of linoleyl alcohol, 0.1 part of tertiary butyl catechol, and 185 parts of tributyl amine are added to 1000 parts of diethyl ether in a suitable container equipped with stirrer, reflux condenser and heating and cooling means; the mixture is blanketed with nitrogen gas through an inlet. To this mixture is added over a period of 2 hours at 20° C., 166.5 parts of vinyl benzoyl chloride in 200 parts of ether, following which the temperature is raised to 30–35° C. for 1 hour. The mixture is then washed with dilute hydrochloric acid, then with water to remove trimethyl amine hydrochloride, followed by washing with dilute aqueous sodium carbonate and again with water until neutral. The resulting ether solution of the ester, $CH_2{=}CHC_6H_4COOC_{18}H_{33}$ is dried over anhydrous Na_2CO_3, decolorized with active carbon and filtered. The monomer is isolated by distilling off the ether at reduced pressure leaving the monomer. Analysis for carbon and hydrogen gives values of 81.79% C. and 10.01% H., which are in good agreement with the theoretical values of the compound. The monomer is polymerizable in pure form or in the ether solution prior to isolation.

When 268 parts of oleyl alcohol are used instead of the linoleyl alcohol, then the corresponding ester (a)

$$CH_2{=}CHC_6H_4COOC_{18}H_{35}$$

is obtained, whereas when 264 parts of linolenyl alcohol is used, then the corresponding ester, (b)

$$CH_2{=}CHC_6H_4COOC_{18}H_{31}$$

is obtained, which on analysis for carbon and hydrogen gives values of 81.54% C and 10.78% H for (a) and 81.9% C and 9.88% H for (b); which are in close agreement with the theoretical values for these compounds. Similarly, when 180.5 parts of

$$\quad\quad CH_3$$
$$\quad\quad|$$
$$CH_2{=}CC_6H_4COCl$$

is used instead of vinyl benzoyl chloride in this procedure, then the corresponding esters,

$$\quad CH_3 \qquad\qquad\qquad CH_3$$
$$\quad| \qquad\qquad\qquad\quad|$$
$$CH_2{=}CC_6H_4COOC_{18}H_{33},\ CH_2{=}CC_6H_4COOC_{18}H_{35}$$

and

$$\quad CH_3$$
$$\quad|$$
$$CH_2{=}CC_6H_4COOC_{18}H_{31}$$

are obtained.

Example II

One hundred sixty-two parts of methyl p-vinyl-benzoate, 133 parts of linoleyl alcohol, 0.5 part tertiary butyl catechol, and 1.5 parts of sodium methylate are heated to 80–100° C. and the methyl alcohol resulting from transesterification is removed continuously in a distillation column until no more methyl alcohol is released. The unreacted sodium is then neutralized with gaseous HCl,

and the NaCl product removed by filtration. The excess methyl p-vinyl-benzoate is removed by distillation, leaving the crude ester, $CH_2=CHC_6H_4COOC_{18}H_{33}$. This is purified by treatment with active carbon and distillation as in the procedure of Example I. The crude ester is also polymerized as such.

Example III

Two hundred seventy-six parts of the anhydride,

$$(CH_2=CHC_6H_4CO)_2O$$

and 266 parts of linoleyl alcohol and 185 parts of tributyl amine are reacted and then isolated according to the procedure of Example I, and the benzoate ester identical to that of Examples I and II is obtained.

Example IV

A commercial product comprising unsaturated fatty alcohols having an iodine value of 125, and a hydroxyl value of 210, containing the following alcohols in the proportions

	Percent
Linoleyl alcohol	53
Linolenyl alcohol	8
Oleyl alcohol	25
(Unsaturated 86%)	
Cetyl alcohol	8
Stearyl alcohol	5
Arachidyl and others	1
(Saturated 14%)	

is substituted for the linoleyl alcohol of Examples I and II. Mixed esters corresponding to the formula

$$CH_2=CHC_6H_4COOR_{dx}$$

are obtained, in which R_{dx}, although embraced by R_d, is used to represent specifically the mixed hydrocarbon groups in the mixed alcohol as shown above.

Example V

Example I is repeated using a mixture of unsaturated fatty alcohols having an iodine value of 170, a hydroxyl value of 210, and containing the approximate composition

	Percent
Linoleyl alcohol	17
Linolenyl alcohol	51
Oleyl alcohol	21
(Unsaturated 89%)	
Cetyl alcohol	6
Stearyl alcohol	5
(Saturated 11%)	

The resultant mixed ester, $CH=CHC_6H_4COOR_{dx}$, is polymerizable.

Example VI

Example IV is repeated using a mixture of unsaturated alcohols comprising oleyl alcohol in the major amounts, and linoleyl, linolenyl, cetyl, and stearyl in the minor amounts with an iodine value of about 90 (known as Adol 85 of Archer-Daniels-Midland), and there is obtained the mixed esters corresponding to the formula

$$CH_2=\overset{R}{\underset{|}{C}}C_6H_4COOR_{dx}$$

Example VII

Under an inert nitrogen atmosphere, to each of fifty parts of linoleyl vinyl benzoate monomer of Example I in five separate reaction vessels is added 50 parts of anhydrous benzene and (1) 0.1, (2) 0.25, (3) 0.50, (4) 1.00, and (5) 1.5 parts of micronized sodium respectively at 25° C., and within about an hour, the solution, due to the presence of styryl-type anions, becomes bluish green, with the dissolution of the sodium. The mixture is agitated for 48 hours at 25° C. and anhydrous HCl gas is then passed into the mixture to remove the color, after which the solid NaCl is removed from the solution by filtration. The resulting solutions of polymer in benzene may be used as such or the polymer may be isolated by removing the solvent by distillation at 15 mm. pressure. The yield of residue is substantially quantitative and all of them are very viscous thick products. The polymer prepared with 0.1 part (0.2% based on the monomer) of sodium initiator is the most viscous and the polymer prepared with 1.5 parts of sodium (3% on the monomer) is the least viscous, and the other polymers prepared with intermediate sodium concentrations have viscosities between these two extremes.

Example VIII

Example VII is repeated in the absence of benzene solvent but at 30° C. for 72 hours to effect better dissolution of the sodium and polymers similar to those of Example VII are obtained.

Example IX

Three hundred twenty-four parts of freshly distilled hydroxyethyl linoleate, $C_{17}H_{31}COOCH_2CH_2OH$, 0.1 part of tertiary butyl catechol, and 185 parts of tributyl amine are added to 1000 parts of diethyl ether in a suitable container equipped with stirrer, reflux condenser and heating and cooling means; the mixture is blanketed with nitrogen gas through an inlet. To this mixture is added over a period of 2 hours at 20° C., 166.5 parts of vinylbenzoyl chloride in 200 parts of ether, following which the temperature is raised to 30–35° C. for 1 hour. The mixture is then washed with dilute hydrochloric acid, then water to remove trimethyl amine hydrochloride, followed by washing with dilute aqueous sodium carbonate and again with water until neutral. The resulting ether solution of the ester is treated according to the procedure of Example I, and there is isolated the monomer

$$CH_2=CHC_6H_4COOCH_2CH_2OOCC_{17}H_{31}$$

When 326 parts of hydroxyethyl oleate are used instead of the linoleate, then the corresponding ester

$$CH_2=CHC_6H_4COOCH_2CH_2OCOC_{17}H_{31}$$

is obtained. When 322 parts of hydroxyethyl linolenate is used, then the ester

$$CH_2=CHC_6H_4COOCH_2CH_2OCOC_{17}H_{29}$$

is obtained, which on analysis gives values of 76.91% C and 8.79 H, which are in good agreement with the theoretical values for the compounds. These monomers are polymerized with similar results by the procedure of Example VII using 0.05% by weight of sodium.

Example X

Three hundred twenty (320) parts of a redistilled commerical product comprising unsaturated fatty acids derived from soyabean oil and containing the following acids in the proportions

	Percent
Linoleic acid	53
Linolenic acid	7
Oelic acid	25
(Unsaturated 85%)	
Palmitic acid	8
Stearic acid	6
Other acids	1
(Saturated 15%)	

are reacted at 150° C. with 44 parts of ethylene oxide in a pressure autoclave at 110° C. in the presence of 1 part of KOH during the course of two hours. The reaction product is cooled, neutralized with acetic acid and flash distilled at 2 mm. pressure. The mixed hydroxyalkyl es-

ters are substituted for the hydroxyethyl linolenate of Example IX, and esters corresponding to the formula

$$CH_2=CHC_6H_4COOCH_2CH_2OOCR_{dx}$$

are obtained, in which R_{dx} represents the mixed hydrocarbon groups in the mixed acids.

Example XI

Example X is repeated using a mixture of commercial unsaturated fatty acids having an iodine value of 170, containing the approximate composition

	Percent
Linoleic acid	18
Linolenic acid	48
Oleic acid	22
(Unsaturated 88%)	
Palmitic acid	7
Stearic acid	5
(Saturated 12%)	

resulting in the mixed esters,

$$CH_2=CHC_6H_4COOCH_2CH_2OCOR_{dx}$$

Example XII

Example X is repeated using a mixture of unsaturated acids comprising oleic acid in the major amounts, and linoleic, linolenic, palmitic, and stearic acids in the minor amounts with an iodine value of about 90, and there is obtained the mixed esters corresponding to the formula, $CH_2=CHC_6H_4COOCH_2CH_2OCOR_{dx}$.

Example XIII

Under an inert nitrogen atmosphere, to each of fifty parts of the

$$CH_2=CHC_6H_4COOCH_2CH_2OCOC_{17}H_{31}$$

monomer of Example X in five separate reaction vessels is added 50 parts of anhydrous benzene and (1) 0.25, (2) 0.50, (3) 1.00, (4) 1.5, and (5) 2.0 parts of micronized sodium respectively at 25° C. Within an hour, the solution, due to the presence of styryl-type anions, becomes greenish, with the dissolution of the sodium. Each mixture is agitated for 48 hours at 25° C., then anhydrous HCl gas is passed into the mixture to remove the color, and the solid NaCl is thereafter removed from the solution by filtration. The resulting solutions of polymer in benzene may be used as such or the polymer may be isolated by removing the solvent by distillation at 15 mm. pressure. The yield of residue in each case is substantially quantitative. All are very viscous thick products. The polymer prepared with 0.25 part (0.5% based on the monomer) of sodium initator is the most viscous, and the polymer prepared with 2 parts of sodium (4% on the monomer) is the least viscous. The other polymers prepared with intermediate sodium concentrations have viscosities between these two extremes.

Example XIV

Example XIII is repeated in the absence of benzene solvent but at 30° C. for 72 hours to effect better dissolution of the sodium and polymers similar to those of Example XIII are obtained.

Example XV

Example I is repeated using instead of

$$CH_2=CHC_6H_4COCl$$

an equivalent amount of the following acid chlorides prepared from the corresponding acids and $SOCl_2$:

$CH_2=C(CH_3)C_6H_4COCl$, $CH_2=CHC_6H_4CH_2COCl$

$CH_2=CHC_6H_4OCH_2COCl$, $CH_2=CHC_6H_3(CH_3)OCH_2COCl$

$CH_2=C(CH_3)C_6H_4OCH_2COCl$, $CH_2=CHC_6H_4CH_2OCH_2COCl$

and the corresponding monomers:

$CH_2=C(CH_3)C_6H_4COOC_{18}H_{33}$, $CH_2=CHC_6H_4CH_2COOC_{18}H_{33}$

$CH_2=CHC_6H_4OCH_2COOC_{18}H_{33}$

$CH_2=CHC_6H_3(CH_3)OCH_2COOC_{18}H_{33}$

$CH_2-C(CH_3)C_6H_4OCH_2CH_2COOC_{18}H_{33}$

$CH_2=CHC_6H_4CH_2OCH_2COOC_{18}H_{33}$

are obtained, which are polymerized by the procedure of Example VII.

Example XVI

Example X is repeated using 132 parts of ethylene oxide instead of 44 parts and there is obtained the monomer $CH_2=CHC_6H_4CO(OCH_2CH_2)_3OOCR_{dx}$, and when 174 parts of propylene oxide is used, there is obtained the monomer

$$CH_2=CHC_6H_4CO(OCHCH_3CH_2)_3OOCR_{dx}$$

both of which are readily polymerized by the procedure of Example VII.

Example XVII

The mixed alcohols of Example IV are reacted with 5 mol equivalent of ethylene oxide by the procedure of Example X and converted to esters by the procedure of Example I and the mixed esters corresponding to the formula $CH_2=CHC_6H_4CO(OCH_2CH_2)_5OCH_2R_{dx}$, are obtained which are shown to be polymerized by the procedure of Example VII.

Example XVIII

The procedure of Example I is repeated using 164 parts of (vinylphenoxy)ethyl alcohol,

$$CH_2=CHC_6H_4OCH_2CH_2OH$$

300.5 parts of $C_{17}H_{33}COCl$ and 185 parts of butyl amine, and there is obtained the monomer

$$CH_2=CHC_6H_4OCH_2CH_2OCOC_{17}H_{33}$$

When 298.5 parts of $C_{17}H_{31}COCl$ and 296.5 parts of $C_{17}H_{29}COCl$ are used instead of the oleyl chloride, the esters, $CH_2=CHC_6H_4OCCH_2CH_2OCOC_{17}H_{31}$ and

$$CH_2=CHOC_6H_4OCOC_{17}H_{29}$$

respectively are obtained.

Example XIX

Example XVIII is repeated using instead of

$$CH_2=CHC_6H_4OCH_2CH_2OH$$

with $C_{17}H_{31}COCl$ the following alcohols,

178 parts of $CH_2=C(CH_3)C_6H_4OCH_2CH_2OH$

208 parts of $CH_2=CHC_6H_4(OCH_2CH_2)_2OH$

236 parts of $CH_2=CHC_6H_4(OCH_2CHCH_3)_2OH$

134 parts of $CH_2=CHC_6H_4CH_2OH$

234 parts of $CH_2=CHC_6H_4CH_2O(CH_2)_6OH$

238 parts of $CH_2=CHC_6H_4OCH_2COOCH_2CH_2CH_2OH$

there are obtained respectively the corresponding monomers

$CH_2=C(CH_3)C_6H_4OCH_2CH_2OCOC_{17}H_{31}$

$CH_2=CHC_6H_4(OCH_2CH_2)_2OCOC_{17}H_{31}$

$CH_2=CHC_6H_4(OCH_2CHCH_3)_2OCOC_{17}H_{31}$

$CH_2=CHC_6H_4CH_2OCOC_{17}H_{31}$

$CH_2=CHC_6H_4CH_2O(CH_2)_6OCOC_{17}H_{31}$

$CH_2=CHC_6H_4OCH_2COO(CH_2)_3OCOC_{17}H_{31}$.

When this procedure is repeated with $C_{17}H_{33}COCl$ and $C_{17}H_{29}COCl$, then the corresponding esters are obtained.

Example XX

The procedure of Example XIX is repeated with the acid chlorides of Example XI, and the corresponding

monomers having a $R_{dx}COO$— ester structure are obtained.

Example XXI

Example XVIII is repeated using 236 parts of

$$\begin{array}{l} CH_2{=}CHC_6H_4OCH_2CHCH_2OH \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad OCOCH_3 \end{array}$$

(prepared by heating 60 parts of CH_3COOH and 176 parts of

$$\begin{array}{l} CH_2{=}CHC_6H_4OCH_2CHCH_2 \\ \qquad\qquad\qquad\quad \diagdown O \diagup \end{array}$$

instead of $CH_2{=}CHC_6H_4OCH_2CH_2OH$). There are obtained

$$\begin{array}{l} CH_2{=}CHC_6H_4OCH_2CHCH_2OCOC_{17}H_{33} \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad OCOCH_3 \end{array}$$

$$\begin{array}{l} CH_2{=}CHC_6H_4OCH_2CHCH_2OCOC_{17}H_{31} \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad OCOCH_3 \end{array}$$

and

$$\begin{array}{l} CH_2{=}C_6H_4OCH_2CHCH_2OCOC_{17}H_{29} \\ \qquad\qquad\qquad | \\ \qquad\qquad OCOCH_3 \end{array}$$

When 146 parts of divinyl benzene monoxide,

$$\begin{array}{l} CH_2{=}CHC_6H_4CHCH_2 \\ \qquad\qquad\quad \diagdown O \diagup \end{array}$$

is used in this procedure, then

$$\begin{array}{l} CH_2{=}CHC_6H_4CH{-}CH_2OCOC_{17}H_{33} \\ \qquad\qquad\qquad | \\ \qquad\qquad OCOCH_3 \end{array}$$

$$\begin{array}{l} CH_2{=}CHC_6H_4CH{-}CH_2OCOC_{17}H_{31} \\ \qquad\qquad\qquad | \\ \qquad\qquad OCOCH_3 \end{array}$$

and

$$\begin{array}{l} CH_2{=}C_6H_4CH{-}CH_2OCOC_{17}H_{29} \\ \qquad\qquad | \\ \qquad\quad OCOCH_3 \end{array}$$

are obtained respectively.

When acids other than acetic acid are used with the starting epoxide, such as benzoic acid, etc., then the corresponding derivative is obtained, as illustrated with the oleate,

$$\begin{array}{l} CH_2{=}CHC_6H_4OCH_2CH{-}CH_2OCOC_{17}H_{33} \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad OCOC_6H_5 \end{array}$$

Example XXII

A mixture of 120 parts of vinyl phenol

$$CH_2{=}CHC_6H_4OH$$

23 parts of NaOH in $C_2H_5OCH_2CH_2OC_2H_5$ are refluxed with 272.5 parts of $C_{17}H_{33}Cl$ for 12 hours. Then the solvent is removed under a reduced pressure of 15 mm., 500 parts of ether are added and the solution filtered to remove salt. The filtrate is washed with water, dried over anhydrous Na_2CO_3, filtered, then decolorized with charcoal, and the ether removed by evaporation. There is obtained the monomer $CH_2{=}CHC_6H_4OC_{17}H_{33}$.

When for the alkene chloride there is used 270.5 parts of $C_{17}H_{31}Cl$ or 268.5 parts of $C_{10}H_{29}Cl$ there are obtained $CH_2{=}CHC_6H_4OC_{17}H_{31}$ and $CH_2{=}CHC_6H_4OC_{17}H_{29}$ respectively.

Example XXIII

The procedure of Example XXII is repeated using 288 parts of $C_{18}H_{33}ONa$ and 142.5 parts of

$$CH_2{=}CHC_6H_4CH_2Cl$$

and there is obtained the monomer

$$CH_2{=}CHC_6H_4CH_2OC_{18}H_{33}$$

Example XXIV

Example XXIII is repeated using 226.5 parts of

$$CH_2{=}CHC_6H_4(OCH_2CH_2)_2Cl$$

(from $CH_2{=}CHC_6H_4ONa$ and $ClCH_2CH_2OCH_2CH_2Cl$), and there is obtained

$$CH_2{=}CHC_6H_4OHC_2CH_2OCH_2CH_2OC_{18}H_{33}$$

Example XXV

In 1000 parts tetrahydrofurane, a Grignard reaction is performed with 142.5 parts of $CH_2{=}CHC_6H_4CH_2Cl$ and 292.8 parts of $C_{17}H_{29}MgCl$ (from $C_{17}H_{29}Cl+Mg$), and the monomer, $CH_2{=}CHC_6H_4CH_2C_{17}H_{29}$ is isolated by evaporation of the tetrahydrofurane by the procedure of Example XXII.

Example XXVI

Example I is repeated using 620 parts of glyceryl dioleate instead of 266 parts of linoleyl alcohol and the monomer $CH_2{=}CHC_6H_4COOC_3H_5(OCOC_{17}H_{33})_2$ is isolated by evaporation of the dry ether solution after treatment with activated carbon.

Example XXVII

The procedure of Example I is repeated using 143 parts of $CH_2{=}CHC_6H_4CH_2N(CH_2COCl)_2$ instead of the vinyl benzoyl chloride and there are obtained the monomers $CH_2{=}CHC_6H_4CH_2N(CH_2COOC_{18}H_{33})_2$

$$CH_2{=}CHC_6H_4CH_2N(CH_2COOC_{18}H_{35})_2$$

and $CH_2{=}CHC_6H_4CH_2N(CH_2COOC_{18}H_{31})_2$ respectively.

When the acid chloride of the N-(ar-vinylbenzyl)-imidodiacetic acid of this example is replaced by other vinylphenyl aliphatic aminocarboxylic acids given in U.S. Patents 2,840,603; 2,875,162; 2,888,441; 2,910,445, then the corresponding monomer esters are obtained.

Example XXVIII

In an inert atmosphere, a mixture of 80 parts of styrene and 20 parts of linoleyl vinyl benzoate of Example I are added to 200 parts of anhydrous benzene, and to this solution is added 1.1 parts of micronized sodium in 1.1 parts of kerosene at 25° C. and allowed to react for 24 hours with slow agitation. The mixture is then neutralized with 2.8 parts of glacial acetic acid and the solution filtered to remove precipitated salts. The copolymer yield is almost quantitative, and the intrinsic viscosity is 0.124. Titration of the copolymer with bromine for unsaturation shows that the copolymer contains about 20% of linoleyl vinyl benzoate in the copolymer.

Example XXIX

The procedure of Example XXVIII is repeated twice using instead of 20 parts of linoleyl vinyl benzoate, 20 parts respectivelp of oleyl vinyl benzoate and linolenyl vinyl benzoate, and the corresponding copolymers of styrene, respectively, of approximately the same molecular weight, are obtained. After filtration of the benzene solutions, they are evaporated at 20° C. at 10 mm. and almost quantitative yields of copolymers are obtained, with ony slight trace of yellow color. The copolymers are soluble in common solvents, such as the ketones, toluene, esters and halogenated hydrocarbons.

EXAMPLE XXX

The procedure of Example XXVIII is repeated using 93 parts of styrene and 7 parts of the ester, $CH_2{=}CHC_6H_4COOR_{dx}$ of Example IV and 2 parts of BuLi (as a 30% solution in ethyl ether) are added under a nitrogen atmosphere to 200 parts of anhydrous benzene at 0° C. for 15 hours, then allowed to heat to room temperature during a period of 3 hours, following which 3 parts of glacial acetic acid is added to neutralize the lithium and the solution filtered. The polymer solution is then poured into methanol and 96 parts of solid, precipitated copolymer is obtaned which, on analysis, indicates a copolymer of approximately 93.1% styrene and 6.9% of the $CH_2{=}CHC_6H_4COOR_{dx}$ monomer. In a

similar manner a 50–50 copolymer is prepared from equal parts of styrene and the ester of Example IV.

Example XXXI

The procedure of Example XXVIII is repeated using 85 parts of butyl methacrylate, 15 parts of the ester, $CH_2{=}CHC_6H_4COOR_{dx}$, of Example IV and 5 parts of finely divided sodium hydride in a sealed reactor which had been degassed and blanketed with deoxygenated nitrogen and the polymerization conducted at −5° C. to 5° C. for 24 hours. The reaction product is then neutralized with 10 parts of anhydrous acetic acid, filtered and then concentrated by distillation at 10 mm. at 25° C., leaving 96.3 parts of a rubbery polymer product.

Example XXXII

The procedure of Example XXVIII is repeated using 65 parts styrene, 25 parts of methyl acrylate and 10 parts of the monomer, $CH_2{=}CHC_6H_4COOR_d$ of Example VI as the monomer feed and the corresponding tripolymer obtained.

Example XXXIII

To ten parts each of the five polymers of Example VII in twenty parts of benzene respectively is added 0.1 part of commercial 10% drier solution containing lead, manganese and cobalt in the approximate ratio of 9.6:1:1.8 as naphthenates. Films of the resultant compositions are prepared on glass plates and the solvent allowed to evaporate at room temperature. On evaporation of the solvent, the residue varies from viscous oily coatings to tacky films, are initially soluble in benzene and acetone, but after seven or eight hours, become converted to dry, substantially colorless, elastic, tough films, insoluble in benzene, acetone and dioxane. When the metallic drier is omitted from the formulation, dry but less elastic films are obtained in 24–36 hours.

Example XXXIV

The procedure of Example XXXIII is repeated with (1) the three polymers of Example IX; (2) the styrene copolymers of Example XXVIII; (3) the styrene copolymer of Example XXIX; (4) the styrene mixed drying oil alcohols-vinyl benzoate copolymer of Example XXX; (5) the butyl methacrylate-copolymer of Example XXXI; and (6) the terpolymer of Example XXXII. In all cases the coatings become converted to benzene-insoluble films in 8–12 hours at room temperature, when the drier is used.

Example XXXV

Linseed oil is heat polymerized at 290° C. under an inert atmosphere for 12 hours. Then the experiment is repeated using a mixture of 90% by weight of linseed oil and 10% by weight of the polymer (2) of Example VII. The viscosities of the stand-oil and polymer-modified stand-oil are compared in Table 2.

TABLE 2

Time in hours	Viscosity of of oil in Process	Viscosity of of Oil plus polymer
1	1.15	3.8
2	1.59	28.6
4	3.5	71.0
6	9.2	152.8
8	24.0	205.4
10	82.0	392.6
12	196.0	
16	390.0	

It will be noted that the addition of polymer to the oil causes a more rapid increase in the viscosity of the resulting stand-oil, and that at least 16 hours of heating are required by the unmodified oil to attain a viscosity equal to about ten hours heating of the polymer-modified oil. The same improvement in a reduction of the time required to prepare stand oils from tung, perilla, oiticica, corn, hempseed, safflower, sandal seed and sunflower oil is observed when the polymers of this invention are added to the oil before heat treatment. Depending on the oil, the modified stand oil is prepared at temperatures varying from 240° C. to 310° C. and for periods of time varying from 1 hour to 12 hours, a factor which is also controlled by the amount of polymer added to the oil, and a reduction in the heating time is noted when the other polymers of Examples VII, VIII, IX, and XXVIII to XXXII are added to oil before or during the heat processing. The modified stand oils can be formulated into varnishes by dilution with solvents to which is added metallic driers, or they may be emulsified after drier addition and used in emulsion form.

Example XXXVI

To fifty parts of a long oil glyceryl phthalate alkyd resin containing 55% of combined linseed oil fatty acids in toluene is added 25 parts of a 50% solution in toluene of the polymer of Example XXXI and the drier content adjusted to 0.1% of metal content on the basis of polymer content. Films of this varnish dry in 2.5 hours whereas films prepared from this alkyd resin are not dry in 5.5 hours. A marked improvement in drying time is also shown when the polymers of Examples VII to IX, XXVIII to XXX, and XXXII are added in various amounts to a long oil glyceryl phthalate alkyd resin; and an even greater improvement is noted when these polymers are added to a short-oil alkyd resin containing about 40% of combined linseed oil fatty acids.

Example XXXVII

Linseed oil of specific gravity 0.9290, and containing 0.05% soluble lead salts and 0.08% soluble manganese salt, is heated to 80° C. while a stream of air is blown through it for 20 hours. A "boiled oil" of gravity 0.940 is thus obtained. When the process is repeated with a mixture of the same oil containing 10% of polymer (2) of Example VII, a boiled oil of the same gravity is obtained in 14 hours.

Example XXXVIII

To 10 parts of the polymer (2) of Example VII is added 6 parts of solid para-phenyl phenol-formaldehyde resins (known commercially as Bakelite—BR 254). The mixture is heated to 220° C. until a clear melt results when a drop is removed and placed on a glass plate. Then the product is dissolved in 35 parts of a solvent mixture of a ratio 2 parts of white spirits to 1 part of toluene, containing 0.1 part of commercial metal driers per part of the polymer. A film cast from this solution dries to a tack-free glassy, water-resistant film in 2–3 hours.

Similar good results are obtained when tertiary butyl phenolformaldehyde resin is used instead of the phenyl-phenol resin.

Example XXXIX

To each of the three monomers of Example I corresponding to the formula

$$CH_2{=}\overset{\displaystyle R}{\overset{|}{C}}C_6H_4COOCH_2R_d$$

is added 1.5% by weight of benzoyl peroxide and the mixture heated at 80–85° C. No noticeable polymerization occurs in 6–8 hours but in 24–48 hours, benzene-insoluble, crosslinked gells are obtained.

Example XL

To a mixture of 90 parts of methyl methacrylate and 10 parts of the linoleyl vinyl benzoate is added 1 part of benzoyl peroxide and the mixture heated to 80–85° C. A benzene and acetone insoluble copolymer is obtained upon maintaining this temperature for 24 hours. Similar

results are obtained when the other two monomers of Example I are used instead of the linoleyl derivative.

Example XLI

To a mixture of 80 parts of styrene and 20 parts of linolenyl vinyl benzoate is added 0.3 part of BF_3 at room temperature. A dark brownish mass, insoluble in benzene, is obtained.

Example XLII

To each of 100 parts of oleyl alcohol, linoleyl alcohol, and linolenyl alcohol is added 0.1 part of the drier of Example XXIII. Glass plates are coated with the respective mixtures. No drying occurs at room temperature in 6 days.

Example XLIII

To 100 parts of linoleyl acetate (prepared from acetic anhydride and linoleyl alcohol) is added 0.1 part of the dryer of Example XXIII, and a glass plate is coated with the mixture as in Example XLII. No drying is observed in 6 days at room temperature.

Example XLIV

To 400 parts of anhydrous liquid ammonia at −77° C. is added 0.1 part of sodium with the formation of a blue color indicating $NaNH_2$ had formed and then is added a mixture of 18 parts of methyl methacrylate and 2 parts of linoleyl vinyl-benzoate to form a solid copolymer which is removed by filtration. The product is washed with 50–50 methyl alcohol-water mixture containing 3 parts HCl, followed by washing twice with a 50–50 methyl alcohol-water mixture, and then dried in vacuo to constant weight. A 95.2% yield of polymer is obtained.

Example XLV

A flat enamel is prepared according to standard procedures in the painting art containing 55% pigment and 45% vehicle in the following proportions.

Total pigment 55% comprising:	Percent
Titanium pigment	57.2
Calcium carbonate	36.0
Diatomaceous silica	4.8
Zinc stearate	2.0
Total vehicle 45% comprising:	
Polymer Example XLIII	20.0
Polymer stand-oil of 395 viscosity of Example XXXV	5.2
Solvent (50–50 mineral spirits-toluene) containing 0.15 part metal driers	74.8

A sized plaster surface is coated with this paint which dries in about three hours to give a very white satin finish with excellent water resistance that can be rewashed repeatedly.

Example XLVI

A commercial acrylic latex paint is applied (without first applying the sizing undercoat recommended when a latex is applied over oil-type paints) to wood previously coated with a drying oil-alkyd type paint and aged for at least 3 months. This new coating is allowed to air-dry for 24 hours and then exposed to weathering. To another part of the same acrylic latex is added 5% by weight of the copolymer of Example XXXI (previously emulsified as a 40% emulsion in water with dodecylbenzene sodium sulfonate) and applied in the same way as the unmodified acrylic latex. At the end of six months, peeling and blistering is observed in the film with the commercial latex, whereas the modified latex coating is continuous and intact. In a similar manner vinyl acetate and styrene-butadiene latices can be modified by the addition of the polymers of this invention to improve their properties.

Example XLVII

A mixture of 70 parts of asphaltic bitumen (M.P. 90° C.) and 30 parts of polymer (2) of Example VII are heated at 100° C. for 15 minutes, then diluted with 70 parts of solvent mixture containing 80% white gasoline and 20% benzene and 0.03 part of metallic driers.

This solution is used to coat tin plate and allow to dry for 6 days. A similar solution of the asphaltic bitumen is prepared without including the polymer of Example VII and air dried for a similar period of time. When both plates are placed in an oven and the temperature raised to 95° C., the coating not containing polymer sags and flows, whereas the solution containing the polymer does not sag or flow. Mixtures of asphaltenes of this type with the polymers of this invention, are particularly suitable for the preparation of gutter paint, rust proofing and water resistant coating for underground pipes of all kinds, including iron, brass, copper, and for exposed metal, ceramic, clay, wood, wall board, concrete and stone surfaces, as well as for the preparation of asphalt shingles, roofing paper, etc. Instead of the asphaltic bitumen, other bitumens such as blown asphaltic bitumens, stearine pitches, Grahamite (an asphaltum from Virginia and Oklahoma), Gilsonite (an asphaltum from Utah), coal tar pitches, etc., can also be modified by the polymers of this invention to improve their flow properties.

Example XLVIII

A mixture of 320 parts of linoleyl vinyl-benzoate and 11.5 parts of sodium are reacted at 50° C. according to the procedure of Example VII and the product isolated. Molecular weight determinations indicate that the product is a dimer. To 100 parts of the dimer is added one part of the drier of Example XVIII and a film prepared on a glass plate therefrom dries in 6–7 hours.

Example XLIX

To 30 parts of polymer (1) of Example VII is added 1.5 parts of sodium dioctyl sulfosuccinate and the mixture heated with agitation at 100° C. until a uniform mixture is obtained, following which there is added 70 parts of water heated to 70° C. and a smooth emulsion is obtained. The addition of metallic driers such as the water-soluble salts of a mixture of cobalt, lead and manganese acetates produces a latex varnish which air-dries within four hours when laid down as a film on glass, iron, and aluminum plates. The latex can be pigmented in the usual way to produce high gloss enamels, satin-finish enamels, or semi-gloss and flat-finish paints; or it can be added to other preformed latex paints such as the styrene-butadiene-, acrylic- or vinyl latex paints to improve their adhesion properties.

Example L

To 150 parts of dry dioxane containing 40 parts of isoprene, 10 parts of ethyl acrylate and 5 parts of linolenyl vinyl-benzoate, cooled to −30° C., is added 0.3 part of BuLi as a 50% solution in ethyl ether and the mixture maintained at this temperature for 16 hours, following which is is neutralized with acetic acid after the mixture is allowed to warm up to room temperature. The dioxane is removed by evaporation at 15 mm. pressure, 120 parts of toluene is added and the resulting polymer solution is filtered.

When metallic driers are added to this solution, and films prepared therefrom, more rapid drying occurs than in a corresponding polymer which contains no linolenyl vinyl-benzoate in its composition.

Example LI

To each of 100 parts of oleic acid, linoleic acid and linolenic acid is added 0.1 part of the drier of Example XXIII and glass plates coated with the mixtures. No drying occurs at room temperature in 6 days.

Example LII

To each of 100 parts of $CH_3COOCH_2CH_2OCOC_{17}H_{33}$ (prepared from acetic anhydride and hydroxyethyl linole-

ate) and hydroxyethyl linoleate is added 0.1 part of the drier of Example XXIII, and glass plates coated with the mixture as in Example XLII. No drying is observed in 6 days at room temperature.

Example LIII

The procedure of Example VII is repeated with the monomers of Examples XV, XVI and XVII and polymerization products are obtained in all cases which air-dry when mixed with the driers of Example XXIII, cast into films and tested as in the procedures of Example LI and LII.

Example LIV

In an inert atmosphere, a mixture of 75 parts of styrene and 25 parts of the ether, $CH_2{=}CHC_6H_4OC_{17}H_{31}$ is added to 200 parts of anyhdrous benzene. To this solution is added 0.05 part of BuLi in 1.1 parts of hexane at 25° C. and allowed to react for 24 hours with slow agitation. The mixture is then neutralized with glacial acetic acid and the solution filtered to remove precipitated salts. The copolymer yield is almost quantitative. Titration of the copolymer with bromine for unsaturation shows that the copolymer contains about 24.6% of the ether monomer in the copolymer. Driers are added to the solution and films prepared by the procedure of Example XXIII which air-dry in about 6 hours. To remove volatile matter, the films are dried in an oven at 70–80° C. for 24 hours, then the films tested with 50% aqueous H_2SO_4, conc. HCl, 10% aqueous NaOH, 20% KOH and they remain unaffected, whereas alkyd resin films similarly tested are degraded.

Example LV

The procedure of Example XLIV is repeated, using instead of 25 parts of the ether, 25 parts respectively of the hydrocarbons

$$CH_2{=}C(CH_3)C_6H_4C_{17}H_{29}$$

and $CH_2{=}CHC_6H_4CH_2C_{17}H_{31}$ and the corresponding copolymers, respectively, of approximately the same molecular weight are obtained, and they are also very resistant to acids and alkali when their films are air dried.

Example LVI

Suitable results are obtained when the procedure of Example VII is repeated a number of times using in place of the sodium equivalent amounts respectively of the following anionic initiators: K, Ca, KH, $(C_6H_5)_3CNa$, $C_6H_5C(CH_3)_2{-}K$, BuLi, $C_6H_5CH_2Cs$, allyl sodium, C_6H_5MgBr, BuMgBr, allyl MgBr, and Na naphthyl.

In the above examples, the polymers have repeating unit structures corresponding to the respective monomers used. For example, in Example I, polymers derived from linoleyl vinyl-benzoate having a repeating unit of the formula

$$-CH_2CH(C_6H_4COOC_{18}H_{33})-$$

polymers derived from the corresponding oleate have a repeating unit of the formula

$$-CH_2CH(C_6H_4COOC_{18}H_{35})-$$

polymers derived from the corresponding linolenyl ester have a repeating unit of the formula

$$-CH_2CH(C_6H_4COOC_{18}H_{31})-$$

polymers derived from the corresponding alpha-methyl-vinyl-benzoates have the repeating units of the following respective formulas

$$-CH_2C(CH_3)(C_6H_4COOC_{18}H_{33})- \qquad -CH_2C(CH_3)(C_6H_5COOC_{18}H_{35})-$$

and

$$-CH_2C(CH_3)(C_6H_4COOC_{18}H_{31})-$$

In example IX, polymers derived from the vinyl-benzoyl esters of hydroxy-ethyl linoleate and oleate, have the repeating unit formulas respectively:

$$-CH_2CH(C_6H_4COOCH_2CH_2OOCC_{17}H_{31})-$$

and

$$-CH_2CH(C_6H_4COOCH_2CH_2OOCC_{17}H_{29})-$$

In Example XVIII, polymers derived from the (vinyl-phenoxyl)-ethyl oleate and from the corresponding linolenate have the repeating unit formulas respectively:

$$-CH_2CH(C_6H_4OCH_2CH_2OOCC_{17}H_{33})-$$

and

$$-CH_2CH(C_6H_4OCH_2CH_2OOCC_{17}H_{29})-$$

In Example XXVI, polymers derived from the glyceryl dioleate ester of vinyl-benzoic acid have the repeating unit formula

$$-CH_2CH(C_6H_4COOC_3H_5(OOCC_{17}H_{33})_2)-$$

Polymers derived from the monomer of Example XXVII have repeating units of the formula

$$-CH_2CH(C_6H_4CH_2N(CH_2COOC_{18}H_{33})_2)-$$

While certain features of this invention have been described in detail with respect to various embodiments thereof, it will, of course, be apparent that other modifications can be made within the spirit and scope of this invention, and it is not intended to limit the invention to the exact details shown above except insofar as they are defined in the following claims.

The invention claimed is:

1. A polymer having the plurality of repeating units in the linear chain thereof having a formula

$$-CH_2C(R)(Ar{-}Z{-}R_d)-$$

wherein R is selected from the group consisting of hydrogen and methyl;

Ar is a radical having no more than 15 carbon atoms selected from the class consisting of phenylene and the derivatives thereof in which each derivative group is selected from the class consisting of alkyl, aryl, cycoalkyl, alkoxy, aryloxy, cycloalkoxy, carbalkoxy, chlorine, bromine, fluorine, $-COOCH_3$, $-COOC_4H_9$; and amino groups;

Z is a divalent radical of no more than 22 carbon atoms connecting said R_d group to said Ar group and contains therein only groups selected from the class consisting of hydrocarbon, —C(O)O—, —O—, —NR— and

$$-N<$$

groups, in which latter four groups the unoccupied valencies are attached to carbon atoms of groups selected from the class consisting of Ar, R_d and a hydrocarbon group of said Z;

R_d is an unsaturated aliphatic radical containing no less than 16 and no more than 24 carbon atoms and consisting of a terminal $-CH_3$ group, at least 1 and no more than 4 —CH=CH— groups, and the remainder consisting of $-CH_2-$ groups.

2. A polymer of Claim **1**, in which said repeating units represent at least 0.1 percent by weight of said polymer.

3. A polymer of claim 1, in which said repeating units represent at least 0.5 percent by weight of said polymer.

4. A polymer of claim 1, in which said polymer also has a plurality of repeating units therein having the formula

wherein Ar' is a monovalent aromatic nucleus.

5. A polymer of claim 1, in which said polymer also has a plurality of repeating units therein having the formula

6. A polymer of claim 1, in which said repeating unit has the formula,

7. A polymer of claim 1, in which said repeating unit has the formula,

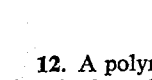
8. A polymer of claim 1, in which said repeating unit has the formula,



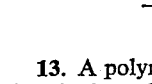
9. A polymer of claim 1, in which said repeating unit has the formula,

10. A polymer of claim 1, in which said repeating unit has the formula,

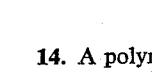
11. A polymer of claim 1, in which said repeating unit has the formula,



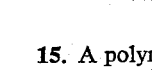
12. A polymer of claim 1, in which said repeating unit has the formula,



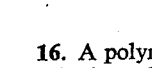
13. A polymer of claim 1, in which said repeating unit has the formula,



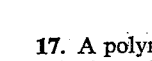
14. A polymer of claim 1, in which said repeating unit has the formula,



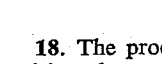
15. A polymer of claim 1, in which said repeating unit has the formula,



16. A polymer of claim 1, in which said repeating unit has the formula,



17. A polymer of claim 1, in which said repeating unit has the formula,



18. The process of preparing the linear polymer comprising the step of polymerizing a monomer having a formula $CH_2=C(R)—Ar—Z—R_d$, said polymerization being effected in the presence of an anionic initiator at a temperature in the range of −80° C. to 80° C., in which formulas

R is selected from the group consisting of hydrogen and methyl;

Ar is a radical having no more than 15 carbon atoms selected from the class consisting of phenylene and the derivatives thereof in which each derivative group is selected from the class consisting of alkyl, aryl, cycloalkyl, alkoxy, aryloxy, cycloalkoxy, carbalkoxy, chlorine, bromine, fluorine, hydrocarbon carboxylate ester, and amino groups;

Z is a divalent radical of no more than 22 carbon atoms atoms connecting said R_d group to said Ar group and contains therein only groups selected from the class consisting of hydrocarbon, —C(O)O—, —O—, —NR— and —N<

groups, in which latter four groups the unoccupied valencies are attached to carbon atoms of groups selected from the class consisting of Ar, R_d and a hydrocarbon group of said Z;

R_d is an unsaturated aliphatic radical containing no less than 16 and no more than 24 carbon atoms and consisting of a terminal —CH_3 group, at least 1 and no more than 4 —CH=CH— groups, and the remainder consisting of —CH_2— groups said anionic initiator being selected from the class consisting of NaH, LiH, KH, CsH, $LiAlH_4$, LiR^-, NaR^-, KR^-, CsR^-, R^-MgCl, R^-MgBr, Li, Na, K, Cs, KNH_2, $NaNH_2$, $LiNH_2$, $Ca(NH_2)_2$, $Sr(NH_2)_2$ and $Ba(NH_2)_2$, wherein R^- represents a hydrocarbon radical of no more than 12 carbon atoms.

19. The process of claim 12, in which said initiator is sodium.

20. The process of claim 12, in which said initiator is butyl lithium.

21. The process of claim 12, in which said initiator is a combination of sodium and liquid ammonia.

22. A compound having the formula $CH_2=C(R)—Ar—Z—R_d$ wherein

R is selected from the group consisting of hydrogen and methyl;

Ar is a radical having no more than 15 carbon atoms selected from the class consisting of arylene radicals and the derivatives thereof in which each derivative group is selected from the class consisting of alkyl, aryl, cycloalkyl, alkoxy, aryloxy, cycloalkoxy, carbalkoxy, chlorine, bromine, fluorine, hydrocarbon carboxylate ester and amino groups;

Z is a divalent radical of no more than 22 carbon atoms connecting said R_d group to said Ar group and contains therein only groups selected from the class consisting of hydrocarbon, —C(O)O—, —O—, —NR— and —N< groups, in which latter four groups the unoccupied valencies are attached to carbon atoms of groups selected from the class consisting of Ar, R_d and a hydrocarbon group of said Z.

R_d is an unsaturated aliphatic radical containing no less than 16 and no more than 24 carbon atoms and consisting of a terminal CH_3 group, at least 1 and no more than 4 —CH=CH— groups, and the remainder consisting of —CH_2— groups.

23. A compound having the formula $CH_2=CH—C_6H_4COOC_{18}H_{35}$

24. A compound having the formula $CH_2=CH—C_6H_4COOC_{18}H_{31}$

25. A compound having the formula $CH_2=C(CH_3)—C_6H_4COOC_{18}H_{33}$

26. A compound having the formula $CH_2=C(CH_3)C_6H_4COOC_{18}H_{35}$

27. A compound having the formula $CH_2=C(CH_3)C_6H_4COOC_{18}H_{31}$

28. A compound having the formula $CH_2=CHC_6H_4COOCH_2CH_2OOCC_{17}H_{31}$

29. A compound having the formula $CH_2=CHC_6H_4COOCH_2CH_2OOCC_{17}H_{29}$

30. A compound having the formula $CH_2=CHC_6H_4OCH_2CH_2OOCC_{17}H_{33}$

31. A compound having the formula $CH_2=CHC_6H_4OCH_2CH_2OOCC_{17}H_{29}$

32. A compound having the formula $CH_2=CHC_6H_4COOC_3H_5(OOC_{17}H_{33})_2$

33. A compound having the formula $CH_2=CHC_6H_4N(CH_2COOC_{18}H_{33})_2$

No references cited.

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