The present invention relates to driers for varnishes, lacquers, oil colors and such plastic masses which contain drying oils and to processes of preparing them.

For the preparation of the driers hitherto usual in the manufacture of varnishes, lacquers, oil colors and plastic masses especially the heavy metal salts, the earth metal salts and the alkaline-earth metal salts of naphthenic acids, resin acids and linseed oil fatty acids are used. The naphthenates are distinguished by their high metal content, their good stability on storage and their good solubility in oils and volatile solvents, but they have a specific odor which in some cases may have a disturbing action. The resins readily oxidize in the air, are relatively sparingly soluble in oils and the usual solvents and partly separate again from these solutions when allowed to stand. The linoleates likewise tend to oxidize and their surface covers with an always increasing layer of linoinx which injures the solubility. The dissolved driers may effect separations and thickenings so that the solutions or mixtures thereof become completely useless.

It has likewise already been suggested to use the mixtures of acids of fractions of these mixtures obtained by the oxidation of paraffin, Montan wax and the like for the preparation of driers for varnishes, lacquers, oil colors and plastic masses. The salts of these acids have a solvency like that of pitch-like consistency. They are only partly soluble in volatile solvents and in their metal content they come only up to the resinates and linoleates but not to the naphthenates.

Furthermore the fatty acids with 6 to 12 carbon atoms in an unbranched chain obtained as first runnings during the distillation of coconut oil or palm oil have been recommended for the preparation of driers. In order to increase the solubility the crude fatty acid salts obtained by precipitation are preferably molten together while adding 2 to 20 per cent. of free unsaturated fatty acid, for instance oleic acid, at temperatures between 100°C. and 200°C. These solutions, too, have the tendency of gelatinizing and an addition of benzoic acid or the like is suggested to prevent this gelatinization.

Now we have found that the above named drawbacks may be avoided and valuable, nearly odorless driers of an excellent solubility in oil and volatile solvents such as benzene are obtained by transforming into simple or complex salts of certain polyvalent metals in a manner known as such the carboxylic acids containing 6 to 16 carbon atoms and branched carbon chains or mixtures of such carboxylic acids or fractions of these mixtures as they may be obtained by an alkaline oxidation at raised temperatures and, if necessary, under elevated pressures from primary alcohols and especially from the mixed alcohols of the abutyl oil obtained as by-product during the synthesis of methanol and boiling at a temperature above 140°C., for instance according to the process described in German Patents No. 503,009 and No. 441,272.

The said carboxylic acid mixture of the so-called isobutyl oil is a clear to weakly yellowish liquid of an average acid number of 290 milligrams to 300 milligrams of KOH whereas the acid numbers of the various fractions are between 300 milligrams and 400 milligrams of KOH. Acid number herein means the quantity of alkali expressed in milligrams which is necessary for the neutralization of the free fatty acid contained in 1 gram of the substance. The main quantity of the mixture consists of the monocarboxylic acids containing more than 6 carbon atoms, preferably 16 carbon atoms. Under a normal pressure these acids distil chiefly between 200°C. and 300°C.

The fatty acids prepared as described above are especially characterized by their carbon chains being branched to a large extent. Whereas the heavy metal salts, earth metal salts and alkaline-earth metal salts of the saturated fatty acids having a normal unbranched carbon chain are sparingly soluble in linseed oil and benzine hydrocarbons, the corresponding salts of acids having a branched chain are distinguished by their good solubility in the said substances. Isocarboxylic acids with relatively short chains may therefore be used as metal carriers; it is possible thereby to chemically bind and keep in solution a large quantity of siccative metal and, therefore, an excellent drying action is attained. Apart from the function of the isocarboxylic acids of causing a dissolution of the siccative metals these additions have still an especially favorable action by improving to a far extent the degree of dissolution and dispersion of the metals in the oils and usual solvents. The metal salts prepared with the aid of these acids yield solutions of a viscosity considerably smaller than that of the corresponding salts with an unbranched carbon chain. This action of the isocarboxylic acids is particularly favorable not only for the acceleration of the drying process but also for the resistance on storage and the stability of the siccative solutions, varnishes and lacquers.

As polyvalent metal salts of the carboxylic acids according to this invention there may be...
used the salts of at least one of the metals cobalt, manganese, lead, zinc, copper, iron, and chromium. The salts of mercury, bismuth, cadmium, cerium, vanadium, and other polyvalent metals are less suitable as they are too expensive.

The preparation of the new driers with the aid of the corresponding acids may for instance be carried out as follows:

1. Precipitation process

The free carboxylic acids are first neutralized with the calculated quantity of alkaline lye at a normal or elevated temperature and the clear alkaline soap solutions, after having been diluted correspondingly, are precipitated, while well stirring, by means of equivalent solutions of salts or metal salt mixtures of at least one of the metals cobalt, manganese, lead, zinc, copper, iron, chromium, aluminum, calcium, etc., in the form of sulfates, chlorides, nitrates, acetates, etc. The precipitates obtained are repeatedly washed, for instance three times, and after the last washing water has been drawn off they are dehydrated by a short melting process up to about 130°C. The dry finely divided lye may then directly be filled into the containers for delivery.

For some purposes already the sodium salts formed during the transformation of the alcoholics or the alcoholic mixture of the isobutyl oil fraction into the corresponding isoacrylic acids may be sufficient. In this case the excess of alkali in the crude soap is neutralized, preferably by means of naphthenic acid, linoleic acid, resinic acid, wool fat acid or other organic acids suitable as metal carriers for driers, advantageously in the heat. The further procedure is as described above. They may, of course, likewise be neutralized by means of other acids, the salts formed, however, must then be washed out.

In order to accelerate and facilitate the melting process and to produce very light and readily soluble products further substances may be added to the precipitated drying-oils, semi-drying oils or non-drying oils or the acids thereof, furthermore the substances called softening agents in the manufacture of plastic masses, such as liquid trialkyphosphates, dialkylphthalates, bismuthnaphthenates, butylate rates or other liquid or readily fusible substances. The period of dehydration may essentially be shortened by the application of a reduced pressure, if desired with addition of small quantities of readily volatile organic solvents such as benzene, toluene, xylene, butanol, etc., and by keeping off air a considerably lighter product may be obtained.

2. Melting process

The free isoacrylic acids are caused to react with the metal oxides or metal hydroxides of the desired heavy metals, earth metals and alkaline-earth metals or with metal salts of volatile acids, such as carbonates, acetates, formates, oxalates or the like at an elevated temperature. In this process there may be used either the oxides or salts of one single metal or simultaneously those of several metals.

3. Direct dissolving process

The free isoacrylic acids are dissolved in mineral spirit, turpentine oil, aromatic, hydroaromatic, chlorinated hydrocarbons and other solvents used in the manufacture of lacquers, such as butanol, butyliacetate, cyclohexanone, etc. Oxides, hydroxides, carbonates, formates, acetates, oxalates or the like salts of the desired siccative metals are caused to react with this solution, while heating and stirring, and the by-products formed such as water, acetic acid, etc. are continuously distilled off.

4. Combined dissolving process

The aqueous solutions of sulfates, chlorides, nitrates, acetates and the like salts of the desired heavy metals, earth metals or alkaline earth metals are mixed, while stirring, with mineral spirit or other volatile solvents, the calculated quantity of an alkaline soap solution of the isoacrylic acids are added, while well stirring, and the whole is stirred, while raising the temperature, until the metal salts formed of the isoacrylic acids are completely dissolved in the solvent.

The process may also be carried out by first precipitating at ordinary temperature by means of alkali lye the metal hydroxides, while keeping off oxygen as far as possible, from the solution of sulfate, chloride, nitrate or acetate applied and then causing these hydroxides to react with the isoacrylic acid added while heating. The driers obtained dissolve at once in the volatile solvent and after a short time they may be separated from the aqueous reaction liquid.

Another variation is to dissolve the isoacrylic acids in volatile solvents and the metal salts in water and to intimately mix these two components and then to add, while well stirring and subsequently heating, the calculated quantity of alkali lye.

Sometimes it may be advantageous to apply the driers prepared accordingly to the above described processes in combination with other driers such as linoleates, resinites, naphthenates, wool grease driers and the like. The isoacrylic acids may also from the beginning be combined with other acids suitable as metal carriers and then be transformed according to the process described into mixed driers. In this case the reaction mostly occurs more rapidly than that with one acid only. Furthermore solubility, stability and drying efficiency of the mixed components is in general substantially improved thereby and the yield of drier considerably increased. The driers described are readily soluble, often already at room temperature or at a temperature raised only for a few degrees, in drying oils and semi-drying oils such as linseed oil, wood oil, perilla oil, soy bean oil or the acids thereof as well as in the usual volatile organic solvents such as mineral spirit, turpentine oil, benzene, toluene, xylene, solvemnaphtha, tetrahydrophthalin, methylene chloride, carbon tetrachloride, cyclohexane and similar synthetic solvents. They form entirely homogeneous solutions which are extraordinarily stable.

The stability and the resistance to storing of the siccative solutions may still be improved by adding to the solutions or already to the solid driers during the preparation small quantities of free carboxylic acids such as crotonic acid or benzoic acid, the substitution products and derivatives thereof containing a free carboxyl group, furthermore amino compounds such as triethanolamine, ethylenediamine, etc. and higher alcohols.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto; the parts are by weight:
2,251,798 (1) 100 parts of isocarboxylic acids prepared by an alkaline oxidation at a raised temperature and, if necessary, under an elevated pressure, for instance according to American Patents No. 503,009 and No. 441,272 from primary higher alcohols, especially from the mixed alcohols of the isobutyl oil obtained during the synthesis of methyl alcohol, which have an acid number of about 300 milligrams of KOH are neutralized at room temperature or while gently heating with a solution of 21 to 22 per cent. caustic soda. The clear soap solution is quantitatively precipitated with a solution of about 76 parts of cobalt sulfate (CoSO₄) 7 H₂O at a temperature below 100°C. The precipitate is repeatedly washed with hot water and dehydrated by melting under reduced pressure. The cobalt drier has a blue-violet color and is very readily soluble in mineral spirit. The yield amounts to 108 to 110 parts with a metal content of 13 per cent. of cobalt.

The manganese drier may be prepared in a shorter manner by precipitation of the above named soap solution with 40 to 41 parts of manganese sulfate MnSO₄. The anhydrous manganese drier has a brown color. The yield amounts to 106 to 108 parts with a content of 12 to 13 per cent. of manganese.

If the above named soap solution is quantitatively precipitated with 69 to 90 parts of lead nitrate Pb(NO₃)₂ 135 to 140 parts of a light yellow lead drier are obtained after washing and dehydrating of the precipitate. The lead content amounts to 34 to 35 per cent. (2) A mixture of isocarboxylic acids with an acid number of 330 milligrams of KOH obtained according to Example 1 is subjected to the fractional distillation. 100 parts of each of the fractions distilling at 10°C. intervals are neutralized with the quinoline of 150 parts of a light yellow lead drier are obtained after washing and dehydrating of the precipitate. The precipitate is twice washed with hot water and dehydrated by a short melting process. The driers obtained for instance from the fractions III, VI and VIII have the following metal contents:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Interval of temperature</th>
<th>Acid number of the acid resin KOH</th>
<th>Pb</th>
<th>Mn</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>III</td>
<td>200-210</td>
<td>419</td>
<td>16.2</td>
<td>12.3</td>
<td>11.3</td>
</tr>
<tr>
<td>IV</td>
<td>210-220</td>
<td>338</td>
<td>15.8</td>
<td>12.8</td>
<td>11.3</td>
</tr>
<tr>
<td>V</td>
<td>220-230</td>
<td>265</td>
<td>12.3</td>
<td>11.3</td>
<td>30.4</td>
</tr>
<tr>
<td>VI</td>
<td>230-240</td>
<td>225</td>
<td>12.3</td>
<td>11.3</td>
<td>30.4</td>
</tr>
<tr>
<td>VII</td>
<td>240-250</td>
<td>205</td>
<td>12.3</td>
<td>11.3</td>
<td>30.4</td>
</tr>
<tr>
<td>VIII</td>
<td>250-260</td>
<td>185</td>
<td>12.3</td>
<td>11.3</td>
<td>30.4</td>
</tr>
</tbody>
</table>

The driers obtained are very light and clear and dissolve very readily in oils and volatile solvents. The solutions have an excellent stability. This surprising solubility is only observed in the case of metal carriers with very branched carbon chains. Driers with a normal unchanged carbon chain containing 30 per cent. of lead or even more do not dissolve in mineral spirit or precipitate again after a short storing.

(3) In 125 parts of the sodium salts obtained during the transformation of higher alcohols, especially the isobutyl oil fraction, into the corresponding isocarboxylic acids and containing 100 parts of free acid with an acid number of 320 milligrams of KOH the excess of alkali is first neutralized with the aid of about 15 parts of sodium carbonate (250 milligrams of KOH). A solution of 103 to 105 parts of lead nitrate Pb(NO₃)₂ is added, while well stirring, and after this reaction is complete a solution of 12 to 13 parts of manganous chloride MnCl₂.4H₂O is added. The lead-manganese drier precipitated in twice or thrice washed in hot water and after the last washing water has been eliminated the drier is kept at about 125°C in a precipitating vessel until the adhering water has completely evaporated.

(4) In a boiler capable of being heated by a direct or indirect firing 100 parts of the isocarboxylic acids with the acid number 310 milligrams of KOH prepared according to German Patents No. 441,272 and No. 503,009 are first heated to 150°C. to 160°C. The temperature is then gradually raised to 210°C. to 220°C. while well stirring, and about 45 parts of manganese acetate Mn(C₂H₅O₂)₂.4H₂O are gradually added in small portions. It is further stirred at this temperature until only a weak odor of acetic acid may be observed. 6 parts of cobaltous oxide hydrate (62 per cent. strength) are then slowly added, while maintaining the temperature, and the whole is further stirred until a homogeneous melt has been formed and a test drop solidifies on a glass plate so as to become transparent.

(5) In a distillation boiler provided with a stirrer 300 parts of mineral spirit are added to 100 parts of isocarboxylic acid with an acid number 380 milligrams of KOH and about 45 parts of lead oxide (92 per cent. strength) and 15 parts of cobaltacetate Co(C₂H₅O₂)₂.4H₂O are introduced into this mixture. The whole is heated, kept well stirring, until water and acetic acid do no longer distill. The reaction is complete after about 2 hours at a final temperature of about 140°C. The cobalt-lead siccative obtained is entirely clear and has a blue-violet color.

(6) An aqueous solution of about 80 parts of manganous chloride MnCl₂.4H₂O is intimately mixed with 200 parts of mineral spirit. 250 parts of the sodium salt of the isocarboxylic acid in an aqueous solution are then slowly added. The reaction occurs already in the cold, while well stirring. The yellow-brown solution obtained contains about 6 per cent. of manganese.

(7) 100 parts of copper sulfate CuSO₄.5H₂O in an aqueous solution are thoroughly mixed with 400 parts of xylene and an aqueous solution of 275 parts of the potassium soap of the isocarboxylic acid serving as a basis for the drier. The xylene solution of the copper salt formed of the isocarboxylic acid is dark green and contains about 4 per cent. of copper.

(8) A solution of 100 parts of the isocarboxylic acids with an acid number of about 300 milligrams of KOH prepared according to German Patents No. 441,272 and No. 503,009 in 200 parts of turpentine oil is intimately mixed with a solution of about 70 parts of zinc sulfate ZnSO₄.7H₂O in 200 parts of water. A solution of about 12 parts of sodium carbonate is then added and the mixture is gradually heated, while well stirring, to about 40°C. until the reaction is complete. The top solution of the zinc salt of the isocarboxylic acid can be separated after some storing and the solvent may be evaporated, if desired.

We claim:
1. Driers for varnishes, lacquers, oil colors and plastic masses of every kind which contain drying oils, the said driers being soluble in oil and volatile solvents, especially benzine and comprising salts which are combinations of at least one metal of the group consisting of cobalt, manganese and lead and aliphatic carboxylic acids which contain from 6 to 16 carbon atoms and a
plurality of branched carbon chains obtained by an alkaline oxidation of primary alcohols at raised temperatures and raised pressures. 2. Driers for varnishes, lacquers, oil colors and plastic masses of every kind which contain drying oils, the said driers being soluble in oil and volatile solvents especially benzine and comprising salts which are combinations of at least one metal of the group consisting of cobalt, manganese and lead and aliphatic carboxylic acids obtained by an alkaline oxidation at raised temperatures and raised pressures of the so-called isobutyl oil obtained as by-product in the synthesis of methanol and boiling above 140° C. 3. Driers for varnishes, lacquers, oil colors and plastic masses of every kind which contain drying oils, the said driers being soluble in oil and volatile solvents especially benzine and comprising salts which are combinations of at least one metal of the group consisting of cobalt, manganese and lead and aliphatic carboxylic acids obtained by an alkaline oxidation at raised temperatures and raised pressures of the so-called isobutyl oil obtained as by-product in the synthesis of methanol and boiling above 140° C. FRIEDRICH MELDERT. EMMERICH v. PONGRATZ. HERMANN SCHATZ.