

ALIEN PROPERTY CUSTODIAN

RESINOUS CONDENSATION PRODUCTS

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vested in the Allen Property Custodian

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The present invention relates to resinous condensation products.

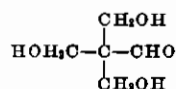
I have found that new synthetic resins are obtained by condensation of saturated aliphatic aldehydes and ketones containing at least two $\text{—CH}_2\text{OH}$ groups at the carbon atom adjacent to the carbonyl group with monobasic or polybasic carboxylic acids. In most cases it is possible to work without condensing agents; catalysts of strong action such as mineral acids are even detrimental. In some cases organic acids of medium strength or the anhydrides thereof may have a favorable influence on the condensation, such as for instance phthalic anhydride, which may also take part in the reaction. As the methylol compounds of aldehydes are starting materials which are readily accessible on an industrial scale (cf. my co-pending U. S. patent application Ser. No. 263,408, filed March 22, 1939), the condensation products are of special importance. The substances obtained show no properties owned by aldehydes or ketones; the free carbonyl group disappears during the condensation, presumably owing to acetalization. This fact probably contributes to the formation of high molecular products suitable as plastic masses.

It is remarkable that one mol of hydroxymethylated aldehyde or ketone esterifies at most with one mol of a monobasic acid with formation of a product with a low acid number. If the one or other component is used in excess, this excess may be distilled off during the reaction or it may be removed unchanged from the mixture after the reaction. When using di-carboxylic acids one carboxyl group remains free. It is not possible to condense this carboxyl group with a further aldehyde or ketone; it may only be condensed with readily esterifiable components, for instance with mono-alcohols or amines, the catalytic action of mineral acid being necessary in the first-named case.

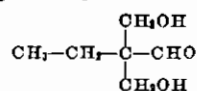
For the condensation there may be used any carboxylic acids of aliphatic or aromatic nature of lower or higher molecular weight, such as for instance acetic acid, propionic acid, butyric acid, caproic acid, heptylic acid, adipic acid, pimelic acid, maleic acid, benzoic acid, phthalic acid, abietic acid, (also in the form of the colophony), furthermore fatty acids from the first runnings obtained in the distillation of paraffin-oxidation products as well as the saturated carboxylic acids obtainable by oxidation of primary saturated aliphatic alcohols in the heat with caustic alkalis or hydroxides of alkali earth metals. As such primary alcohols there may, for instance, be

named the oily alcohol mixtures obtainable in the hydrogenation of carbon monoxide with application of pressure. The acids obtainable from these mixtures in the afore-mentioned oxidation essentially consist of aliphatic saturated acids of the constitution $\text{C}_5\text{H}_{10}\text{O}_2$ to $\text{C}_6\text{H}_{12}\text{O}_2$, they are presumably branched in neighbouring position to the carboxyl group. For the condensation there are further useful the anhydrides of all the above-named carboxylic acids, especially those of the dicarboxylic acids.

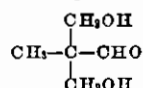
As the other component there may be used for instance: trimethylol acetaldehyde of the formula:



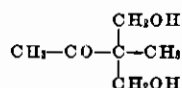
dimethylol butyraldehyde of the formula:



dimethylol propionaldehyde of the formula:



as well as the aldehyde containing hydroxymethyl groups which is obtainable from acetaldo and formaldehyde. All these compounds may be prepared according to the statements in my co-pending U. S. application Serial No. 263,408, filed March 22, 1939. The ketones containing $\text{—CH}_2\text{OH}$ groups which are obtainable according to the same process are not so highly important, for instance:



The condensation is suitably carried through at temperatures between about 100°C to about 200°C . In order to promote the removal of the water formed agents may be added which form with it azeotropically distilling mixtures, for instance toluene or xylene. Furthermore solvents such as butanol may be present.

According to the composition and the degree of condensation the resinous products are obtained in different states ranging from viscous oils to nonpliable or elastic resin. Their solubilities and their properties are of great variety as could be expected. The products are not only important in the field of plastic masses, but they are in part

also useful as textile adjuvants. They are especially suitable as starting materials for varnishes, lacquers and coatings.

The following examples serve to illustrate the invention but they are not intended to limit it thereto:

(1.) 120 grams of trimethylolacetaldehyde are slowly heated to boiling together with 300 grams of glacial acetic acid and 200 grams of toluene. The water which has been formed is distilled off with the toluene and separated therefrom. Thereafter the toluene is returned and distilled off several times until water passes over no longer. Finally the resin formed is freed under reduced pressure from all volatile constituents. For final purification it is treated with sodium carbonate solution and water and dried. 155 grams of a yellowish soft resin having the acid number 6 and the ester number 452 are obtained.

(2.) 110 grams of trimethylolacetaldehyde are heated within 30 hours to 180°C together with 150 grams of colophony WW and 200 ccm of xylene. In order to remove the excess of colophony, the solid resin is treated with ether. A light-yellow powder having the acid number 35 is obtained.

(3.) 344 grams of a fatty acid from the first runnings obtained in the distillation of paraffin-oxidation products with essentially unbranched length of chain of 6 to 9 carbon atoms are heated to 150°C with 240 grams of trimethylolacetaldehyde whereby homogenization occurs and the condensation is started. For finishing it, the temperature is then raised to 180°C (8 hours). In order to deacidify the product it is treated with sodium carbonate solution and then with water and dried. 410 grams of a yellowish, thick, resinous oil of the acid number 1.2 are obtained. From the sodium carbonate solution there are precipitated by means of acid 60 grams of an acid product containing a fatty acid from the first runnings obtained in the distillation of paraffin-oxidation products, which product may be used again.

(4.) 356 grams of a fatty acid from the first runnings obtained in the distillation of paraffin-oxidation products (according to Example 3) with an average molecular weight of 130 are mixed with 450 grams of an aqueous solution of trimethylolacetaldehyde of 80 per cent strength in which 30 grams of phthalic anhydride were previously dissolved in the heat and the water is distilled under reduced pressure. In order to effect the condensation, the temperature is raised first to a value above 100°C and then slowly under reduced pressure within 30 hours up to 180°C until water is no longer formed. The mixture is then dissolved in benzene, freed from acid with sodium carbonate solution and dried. A honey-yellow soft resin of the acid number 13 is obtained which is soluble in aromatic and aliphatic solvents. Instead of phthalic acid maleic acid may also be used for the condensation.

(5.) 274 grams of a fatty acid from the first runnings obtained in the distillation of paraffin-oxidation products are slowly heated under reduced pressure with 264 grams of dimethylolbutyraldehyde to 180°C. A resin is obtained which

is nearly equal to the product obtained according to example 3, but has a somewhat softer consistency.

(6.) 60 grams of trimethylolacetaldehyde are heated for 6 hours to 130°C together with 50 grams of phthalic anhydride. In order to remove the excess of phthalic acid the mixture is treated with benzene. The remaining glassy-brownish resin has an acid number of 203 and a saponification number of 413. It dissolves in cold caustic soda solution without saponification.

(7.) From a mixture of 75 grams of adipic acid and 120 grams of a solution of trimethylolacetaldehyde of 50 per cent strength the water is slowly evaporated within 15 hours and then heated for 2 hours to 160°C to 180°C. The originally turbid mass frothes, clears up and becomes more viscous. 90 grams of a resin are obtained which is insoluble in organic solvents, after cooling has a viscous elastic consistency, dissolves in cold dilute caustic soda solution, is precipitated again by means of an acid but saponifies by a prolonged heating with caustic soda solution and may then no longer be precipitated by means of an acid.

(8.) 150 grams of adipic acid are heated under a pressure of 100 to 200 mm with 320 grams of trimethylolacetaldehyde and 300 grams of a mixture of butanol and xylene for 18 hours to 120°C and the water is azeotropically distilled off. The resin is then treated with warm water for removing the adipic acid in excess and dissolved in butanol. 570 grams of a solution of butanol of the acid number 51 are obtained. This solution is heated with 136 grams of octadecylamine for 4 hours to 100°C. By evaporation a brown semi-soft product is obtained which has valuable textile-chemical properties.

(9.) 100 grams of a soluble condensation product from equimolecular quantities of maleic acid and trimethylolacetaldehyde (condensed at 100°C) of the acid number 201 and of the saponification number 436 are heated together with 200 grams of butanol, 100 grams of formaldehyde of 30 per cent strength, 80 grams of cetyl alcohol and 10 ccm of concentrated hydrochloric acid for 20 hours to 80°C, the aqueous part is then eliminated and the resin is heated for 10 hours at 130°C. After removal of a small excess of cetyl alcohol 155 grams of a thick oil of the acid number 10 is obtained.

(10.) 50 grams of phthalic anhydride are dissolved at 100°C in a solution of 600 grams of trimethylolacetaldehyde in 400 grams of water and then 580 grams of 2,4-dimethyl pentanic acid-1 (isooheptylic acid) are added and the water is slowly distilled off while stirring under reduced pressure. The temperature gradually rises to 180°C. When the evolution of water vapor and consequently the condensation is finished the mixture is freed from acid by treatment with dilute caustic soda solution and then washed with water and dried. A brownish, slightly sticky resin, soluble in aromatic solvents is obtained.

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