

# UNITED STATES PATENT OFFICE.

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## MANUFACTURE OF VARNISHES, BALSAMS, AND RESINS.

No. 848,401.

Specification of Letters Patent.

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*To all whom it may concern:*

Be it known that I, ABRAHAM KRONSTEIN, doctor of philosophy, a subject of the Emperor of Austria, residing at Karlsruhe, Baden, in the Empire of Germany, have invented certain new and useful Improvements in the Manufacture of Varnishes, Balsams, and Resins, of which the following is a specification.

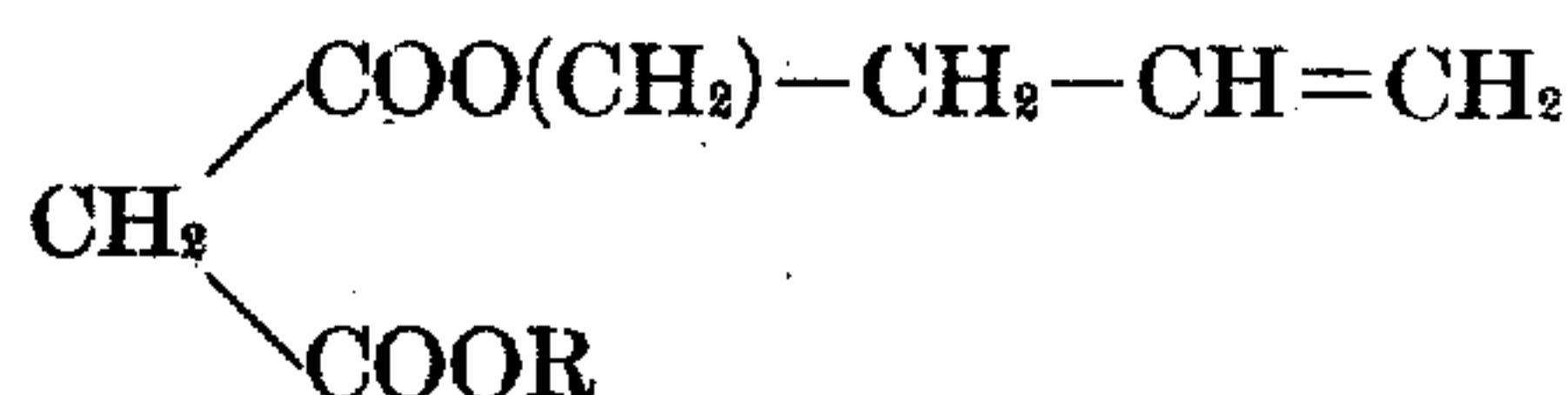
The artificial, as also the natural, thickening of oils—i. e., the formation of varnishes, balsams, and resins and the production of solid oils for the purposes of manufacturing linoleum—has heretofore been considered as mainly an oxidizing process, which is in some cases combined with evaporation. (*Muspratt*, fourth edition, Vol. 4, page 7.) The processes heretofore employed for the manufacture of varnishes have almost entirely been based upon application of oxidizing agents. These oxidizing agents consist either of solid substances giving off oxygen or of air in combination with carriers of oxygen or even of air alone.

In consequence of scientific researches made by me I have come to the conclusion that the above-mentioned assumption is not in accordance with facts. I have discovered that the thickening of oils can be carried out not only in the complete absence of air or other oxidizing agents, but also in the presence of carbonic acid, hydrogen, nitrogen, or illuminating-gas. The products obtained, which are free from oxidation products, are distinguished from varnishes made according to customary processes by their absolute purity. In consequence hereof the improved process is of considerable importance in avoiding complicated and expensive purifications, as also in affording a much greater yield. According to my invention the manufacture is carried out in such manner that the substances to be thickened or the mixtures of several oils are heated, preferably, in closed vessels—that is, practically under exclusion of air to a moderate temperature below that at which decomposition commences.

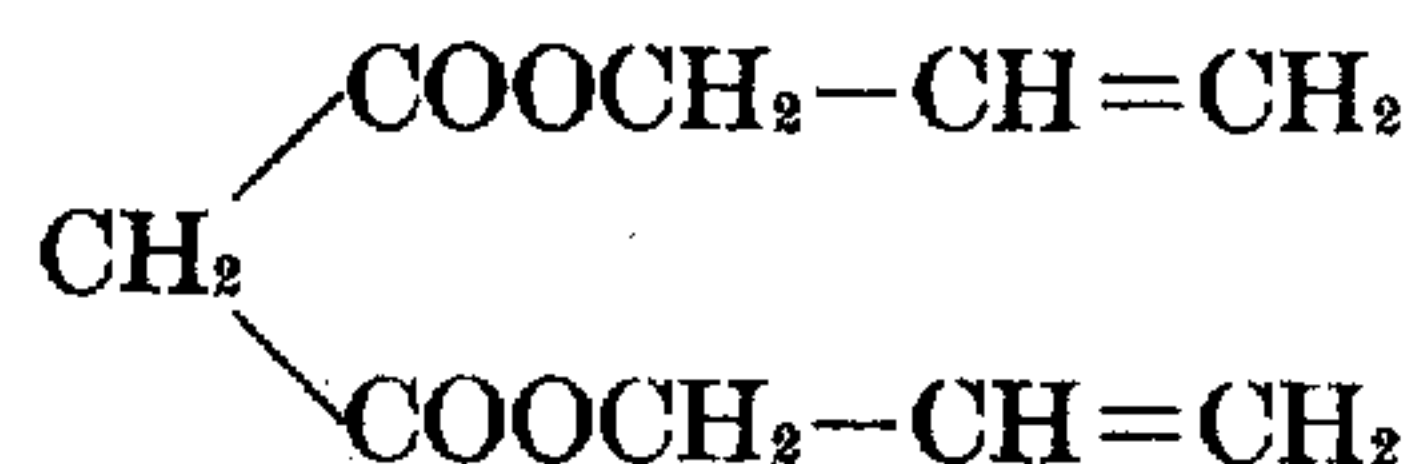
The thickening process discovered by me takes place in three subsequent reaction phases. In scientific as well as in technical respects these three reaction phases will now be described in detail.

*First reaction phase.*—The thickening is to be considered as the first part of the reaction

as long as the products remain in a liquid condition at ordinary temperature or are completely liquefied after a short heating up to 250° centigrade and dissolve in one or more solvents without heating during several hours. I have found that all the unsaturated oleaginous compounds and similar substances named hereinafter undergo this change if they contain in addition to one unsaturated group one or three or more remaining negative groups, such as  $C_6H_5COOH$  or other double groups; but if there are only two negative remaining groups they must have an unsymmetrical disposition with respect to the unsaturated compound or group. Experiments have been made with allyl-cinnamate, mono or diallyl malonate



(R being any suitable alcohol radical)



eugenol, safrol, heavy camphor-oil, styracin, (Chinese) wood-oil, linseed-oil, camelina-oil, rape-oil, cotton-oils, maize-oil, &c. Inasmuch as the so-called "vegetable" drying-oils are composed of ether combinations of organic unnaturated acids with alcohol radicals, it is but natural that artificial products of the same class, such as allyl-cinnamate and allyl-malonate, are capable of undergoing the same change if treated according to my invention as the above-mentioned natural oils. The products of this reaction phase are varnishes, balsams, and soft resins.

*Second reaction phase.*—In the second reaction phase, which takes place after a long heating, the liquid state disappears. The products are at ordinary temperature, as well as at a temperature of 250° centigrade—in the most cases at still higher temperature—solid, soft, more or less elastic, gum-like bodies which in the beginning of the second reaction phase are also viscid. These products are normally insoluble in all solvents and they obtain the property of dissolving only by melting or heating for some time in the presence of the solvent. They behave, therefore, like the hard resins, amber, copal,



&c. They are fit for the manufacture of linoleum, for the production of fine constant lacquers, &c.

There is in particular to be pointed out the fact that the presence of resins—such as cowrie-copal, colophony, and cork-powder—does not impede the course of the reaction.

Products of the second reaction phase are obtained from allyl-cinnamate, diallyl-malonate, &c. Of the natural oils of commerce only wood-oil (termed also "holzöl") yields products of the second reaction phase, while the other natural oils, heated separately, do not produce such products.

*Third reaction phase.*—If the products of the second reaction phase are further heated, they lose their soft, elastic, gum-like state and become solid brittle bodies, which behave as the natural resins. I have found that all the products of the second reaction phase undergo the third and last change, with the exception of the product of wood-oil, which does not completely lose its elasticity. The thickening process can be carried out at any temperature, the latter only having an influence upon the rapidity of the process. By varying the duration of the process and the temperature the products of the several reaction phases can be obtained. With the exception of the resin obtained from benzaldehyde by oxidation, by Hlasawitz, Barth, and Pfaunder (see *Muspratt*, as above) no process has heretofore been made known for obtaining bodies which entirely correspond to the natural resins in the same manner as the products of the second and third reaction phase above described.

As my improved process is carried out under exclusion of oxidizing agents the products are not oxidation products. They frequently surpass natural resins in regard to their purity. The yield is equal to the amount of raw material employed.

#### Examples.

*I. Example for the manufacture of varnish.*—Ten kilograms of linseed-oil are maintained in a closed enameled vessel by means of a bath at a constant temperature of 200° centigrade. The heating can be effected either in the presence of illuminating-gas or carbonic acid or nitrogen or hydrogen. After a heating of thirty-six hours the separation of albumen is finished. The oil is filtered and further heated under the same conditions. After four days the product will be found after cooling to correspond completely to the varnish of commerce known as "standöl." The quantity produced is ten kilograms.

*I<sup>a</sup>. Example for the manufacture of fast lacquers.*—Ten kilograms of oil which have been freed, as described in Example I, from albumen are further heated with the desired quantity of copal, amber, or with the

products of the second or third reaction phase, exactly in the same manner as described in Example I.

The resins above mentioned and the products of the second or third reaction phase may also be dissolved by heating them with turpentine-oil, camphor-oil, &c., and mixed with the linseed-oil thickened according to Example I.

*I<sup>b</sup>. Example for the manufacture of spirit lacquers or varnishes.*—(1) Ten kilograms of the products of the second or third reaction phase or also (2) ten kilograms of the oils which are fit to produce the above said products are heated with volatile liquids—such as turpentine-oil, light camphor-oil, benzol, &c.—in closed vessels to a temperature of from 190° to 250° centigrade until either the products (1) have been dissolved or the oils (2) have attained the desired thickness.

*II. Example of balsam.*—Ten kilograms of allyl-malonate are heated to 170° centigrade in a closed enameled vessel. At the end of twenty-four hours the oil will be thickened and will have the properties of a natural balsam. The yield is ten kilograms.

*III. Example for the production of hard resins.*—Ten kilograms of allyl-cinnamate are heated in a closed enameled vessel first for thirty-six hours to 170° centigrade, after which the temperature is raised to 230° centigrade. After maintaining this temperature for thirty-six hours the process is completed. The resulting product has the appearance of natural amber. It has about the same degree of hardness and can be worked in the same manner. It also behaves in the same manner in the presence of organic and inorganic reagents. The yield is ten kilograms.

In place of the original substances the balsams produced according to Example II may also be employed for manufacturing resins.

*IV. Example for the production of soft resins.*—Ten kilograms of eugenol are heated in a closed enameled vessel to a temperature of 180° centigrade for twenty-four hours. After cooling, the product, which will be ten kilograms, will be a solid substance which corresponds in every respect to the natural soft resins. Like these, it is soluble in alcohol and ether.

I am aware that heating in air-tight vessels has already been employed for resinifying linseed-oil by heat; but this is entirely different from my invention, inasmuch as in the process referred to the oil was heated so as to form a foam and to emit bubbles and increase in volume, which is due to a decomposition of the oil and which may finally lead to solidification, while when treated according to my process, however, no such frothing or foaming takes place, and decomposition is carefully avoided, so that in the case of linseed-oil no solidification even on prolonged heating takes place, the substances submitted to



my new process being heated only at a temperature below the point at which decomposition sets in and which is previously ascertained in every particular case by a separate test with a small sample of the substance under treatment, the temperature of treatment according to my process being preferably about 80° centigrade below the temperature of decomposition.

10 Having thus described my invention, I claim as new and desire to secure by Letters Patent—

1. The process of producing insoluble solid resin and balsam like bodies from allyl-cinnamate which consists in heating a sample of the same to ascertain the temperature of decomposition and then heating the bulk of the substance below this temperature and in the absence of oxidizing agents until solidification and insolubility is reached.

2. The process herein described of producing insoluble solid resin and balsam like bodies from allyl-cinnamate, which consists in ascertaining the temperature at which said allyl-cinnamate is decomposed, and continuously heating said allyl-cinnamate to a temperature below the temperature of decomposition and in the absence of oxidizing

agents until the substance is solidified and rendered insoluble.

3. The process of producing insoluble solid resin and balsam like bodies from organic ether soluble unsaturated ester-like compounds which consists in heating a sample of the compound to ascertain the temperature of decomposition and then heating the bulk of the substance below this temperature and in the absence of oxidizing agents until solidification and insolubility is reached.

4. The process herein described of producing insoluble solid resin and balsam like bodies from organic ether soluble unsaturated ester-like compounds, which consists in ascertaining the temperature of decomposition of the same, and then heating the compound below this temperature in the absence of oxidizing agents until solidification and insolubility result.

In witness whereof I have hereunto signed my name in the presence of two subscribing witnesses.

ABRAHAM KRONSTEIN.

Witnesses:

JACOB ADRIAN,  
JOHN RENSCH.