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THE MANUFACTURE OF MODIFIED, HEAT-BODIED OIL PRODUCTS

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My invention broadly relates to the treatment of natural and industrial artificial isocolloid substances containing unsaturated carbon compounds, that is, organic isocolloids, to modify the physical properties thereof, such as the viscosity, etc., by processes involving colloidal transformations, as more fully hereinafter set forth and as claimed.

In my copending application Serial No. 359,425, which is a continuation-in-part of the present application and which sets forth further embodiments of my generic invention, I broadly claim my generic invention. The present application is directed to certain embodiments of my generic invention, namely, the manufacture of modified heat-bodied oil products from fatty oils by the processes herein claimed.

By "isocolloid substances" I mean colloidal substances whereof the dispersed phase and the dispersion medium of the colloidal system are both of the same chemical composition but, of course, in a different physical state. Such isocolloidal systems are able to enrich the dispersed phase, while the amount of the dispersion medium will be reduced accordingly. For instance, linseed oil and like fatty oils are typical naturally occurring substances of this type and when they are heat-bodied or polymerized, the dispersed phase is enriched, the heat-bodied or polymerized oil having a higher viscosity than the natural oil.

Now, in studying the drying of fatty oils such as linseed oil, I have found that colloidal transformations play an important part in the physical changes incident to the drying of such oils. By "colloidal transformation" I means those changes which occur in the colloid system of the body involving an alteration in the number and size of the colloid aggregations (micelles), which result in a modification of the physical properties of the body, such as viscosity, melting point, elasticity, etc. See "Farbenzeitung", Berlin, 1926, vol. 22, "Chemische Umschau", Stuttgart, 1926, vol. 18, and "Kolloid-Zeitschrift" XL, vol. 4, 1926. By continuing my studies in this direction, I have further discovered that colloidal transformations are also of great importance in modifying other organic isocolloids such as mineral cylinder oils, resins, etc., as well as in the case of fatty oils.

That is, I have found that not only the fatty oils but natural and industrial organic materials, containing unsaturated carbon compounds and of isocolloid nature, in general are susceptible to those colloidal chemical reactions involving colloidal transformation; for instance, resins, oils

including fatty and mineral oils, etc. And I have succeeded by colloidal chemical processes in increasing or in reducing the viscosity of such materials by the present invention. I have found, for instance, that thick oil-like products and even solid substances like hard rubber can be obtained from thin oils. I have further found that resins, either soft or liquid or of any intermediate stage of viscosity or hardness may be obtained from solid resins. In the case of resin-like products, which as is known are solid at ordinary temperature, the increase of viscosity, that is to say the process of solidification, is indicated by the increase in the point of fusion of the products treated, whereas in the case of liquefaction, a considerable reduction or lowering of the point of fusion is noticeable.

Thus by my investigations, I have found that the viscosity and other physical properties of isocolloid substances containing unsaturated carbon compounds and which are either liquid or fusible or thermoplastic, may be substantially modified by altering the structure of isocolloid, the said alterations being effected by interaction between the isocolloid substance and certain electrolytes (polar materials), the electrolyte or polar compound being dispersed or dissolved in the starting material or organic isocolloid to impart polarity to the isocolloid system thereof, and thus producing the desired modification and alteration of its physical properties as more fully hereinafter shown.

In the practice of my invention, I may employ as the electrolyte or polar compound, salts, acids and organic metal compounds, either separately or mixed. I find that metal salts of inorganic and organic acids are advantageous and illustrative examples of each are given post. Also I may employ the acids themselves, particularly an organic acid as illustrated post. Likewise I may employ mixtures of those electrolytes as stated ante.

The electrolyte, which should be added in small quantity, generally not more than a few per cent and in dry form, i. e. free from water, should be dispersed, i. e. dissolved as completely as possible in the substance to be treated by maintaining the mixture at a suitable temperature. The temperature of the reaction chamber should be, however, lower than the boiling point of the raw material used. The degree of heat necessary depends upon the nature of the substance under treatment, and also upon the solubility of the electrolyte in that substance. The complete dispersion, molecular or colloidal, of the

electrolyte in the substance to be treated and modified is an essential element of the process.

That is, in the broad practice of my invention, the electrolyte is incorporated in the raw or starting material, namely, the organic isocolloid, in any suitable manner.

For instance, the organic isocolloid (raw or starting material) and the electrolyte (modifying agent) may be mixed cold; that is, at room temperature, when the electrolyte is directly soluble in the organic isocolloid. Again, they may be simply melted together or fused into a homogeneous mass, if both are readily fusible and miscible with each other. Further, the starting material and electrolyte can be boiled, that is, heated at elevated temperatures such as 300–350° C. if desired and this is advantageous when the electrolyte is difficultly soluble in the particular organic isocolloid being modified. Likewise, in some cases, it is advisable to continue the heat treatment, after the dissolution of the electrolyte is complete and in this way marked modification of the fatty oil or other organic isocolloid may be obtained.

Incorporation of the electrolyte in the organic isocolloid by any of these methods produces substantial modification of its properties. That is, my processes may be practiced in the absence of any additional material, other than the electrolyte. However, I have found that it is advantageous in some cases to incorporate the electrolyte in the presence of additional materials which facilitate its incorporation and the modification of the organic isocolloid. For instance, the electrolyte may be incorporated in the presence of various organic bodies such as the purely organic additions mentioned post. Again metal soaps or siccatives such as used in the varnish industry may be present, for instance, resins and linoleates of metal compounds and metal oxides. Further, sulfur or sulfur compounds, such as for instance, sulfur chloride, may also be present in these processes. The sulfur compounds further modify the products obtained as more fully shown post.

As these processes may be carried out in various ways, the heating may be effected in open or closed vessels as desired. In the latter case, the air can be entirely or partially displaced by another gas. Again, in both cases the gas may be passed through the material being treated. That is, the reaction can be carried out during the passage of a gas. The gas pressure can be that of atmosphere. In many cases, however, a vacuum may be used with advantage as illustrated post. Again, even a higher pressure of several atmospheres is to be recommended in certain cases, it sometimes being advantageous, particularly when the electrolyte has substantially vapor pressure at the temperature employed.

That is, I have further found that the results of the process vary with the nature of the gas present in the reaction chamber and also with the physical condition (pressure) of this gas. Thus I have found that a certain given starting material which is initially liquid will become viscous only as the result of the electrolyte treatment, if the latter is effected under atmospheric pressure (e. g. in an open vessel), but solid if the gas is rarified by the employment of a partial vacuum. In other cases the converse applies. When plus pressure was used the results differed again. Air gives a different result from another gas or a mixture of gases.

The electrolyte treatment may be carried out either in the total or partial absence of air, replacing the same with another gas.

The pressure during the electrolyte treatment may be varied to obtain the best results in each particular case. A pressure treatment followed by a vacuum treatment may be used. I have found it to be advantageous to use alternately, atmospheric or plus pressure and vacuum treatment. Such alternate treatment increases the uniformity of the distribution of the electrolyte. In my process, the gas may be blown or passed through the liquid reaction mass or simply pass over the surface of the same. It is advisable in some cases, both when open or closed reaction vessels are used, to have a constant passage of the gas during the reaction.

It may be stated with reference to the action of gases, that generally speaking rarefaction of the gases present in the reaction chamber by reduction of pressure tends to intensify their action in the process both in the case of solidification of the initial material and also in the case of liquefaction thereof.

With regard to the electrolyte treatment, the actual mechanism of action of the electrolytes is not known, but it has been established that anions as well as cations may be used which are similar to the ion series as identified by Hofmeister and Spiro in the coagulation of albuminous brine see "Leitfaden der Kolloidschemie" Hans Handowsky, Dresden, 1925, pp. 106, 107, 143, 145, 159; also "Die Grundlagen der Dispersionschemie". Andor Fodor, Dresden, 1925, pp. 43, 182, 231, 239. It may also be added that experiments have been made with the ions of ammonium, potassium, sodium, iron, aluminum, calcium, cobalt, lead, antimony, manganese, etc., as cations; and ions of carbonate, tartaric acid, oxalic acid, acetic acid, formic acid, hydrochloric acid, hydrobromic acid, hydriodic acid, sulphuric acid, sulphurous acid, hydrosulphuric acid, thiosulphuric acid, nitric acid, nitrous acid, citric acid, hydrocyanic acid, salicylic acid, naphthalene sulphonic acid, sulphanilic acid, naphthenic acid, thiocyanic acid, etc., as anions. Generally speaking, however, it may be said that cations are more effective than anions and I usually employ metal salts as the electrolyte in my processes. However, in certain cases, acids may be used, particularly organic acids. The acids may be employed also in conjunction with salts and organic-metallic compounds. As stated previously, the metal salt or other electrolyte should be added to the substance to be treated in dry form, that is, added to the reaction mass in the form of a dry powder to facilitate the complete dispersion of the electrolyte in the starting material. It is advantageous to mill the dry electrolyte with the starting material using any of the usual mills or mixers for producing colloidal dispersion. Then the mixture can be subjected to further treatment such as heating if desired.

The temperature of the reaction chamber which gives the best results is that considerably above room temperature and below the boiling point of the raw material used. In certain cases, however, the reaction takes place at low temperature, for instance, at room temperature. In the latter case, the reaction is favorably effected by an excess of pressure, for instance, carrying it out in molds under pressure. In any case, the temperature and time of heating depends upon the starting materials and the results desired.

Experience has shown that the process may

be made to effect either a solidification, or a liquefaction of the initial material. The result, namely, solidification on the one hand, or liquefaction on the other, depends in any given case upon the duration of the heat-treatment of the material, quality, quantity and pressure of the gases present in the reaction chamber, and the quantity and quality of the dissolved electrolyte employed.

If desired, the electrolyte may be produced in situ within the mass of the substance under treatment by interaction within the substance, of substances capable of reacting under the conditions of the process to produce the electrolyte. The same applies to the gas in the presence of which the material is subsequently treated: a substance or substances may be added to the initial material evolving gas during the process. It may be stated that it has been found in certain cases that electrolytes and gases which are produced in situ in the reaction mass and, therefore, in a nascent state, are somewhat more active than those which are added in an already existing and pre-formed state.

If the starting substance is not a naturally occurring material, but has to be produced before it can be treated, it may be advantageous to combine the production process with the treatment with electrolytes.

In addition to the action of electrolytes and the cooperating action of gases in effecting the colloidal transformation characteristic of my invention, an additional modification of the ultimate physical properties of the treated product can be effected by the addition to the substances under treatment of purely (i. e. metal-free) organic bodies, e. g., phenols, naphthols, naphthalene, chloroform, acetone, alcohols and their homologues and derivatives. It is to be understood, however, that the addition of these bodies is supplemental only and not alternative to the use of electrolytes.

Furthermore, siccatives, such as are employed in the varnish industry, may be added in addition to the electrolyte if it is desired to reduce the stickiness of the ultimate product.

According to a further feature of my invention, solid coherent and elastic products may be obtained, similar in general characteristics to ordinary rubber, by adding sulphur to the initial substance, in addition to the agents already mentioned. The sulphur may be added as such, or in the form of a sulphur compound, e. g., sulphur chloride. It would appear that the action of the sulphur is analogous to that which takes place in the vulcanization of rubber. Also, the sulfur or sulfur compounds may be added to the material after the main reaction of the process has been completed; that is, the treatment with sulfur or sulfur compounds can be effected if desired in a second stage or subsequent treatment.

I have also found that the colloidal transformation which takes place by the process according to this invention may be promoted by the use of rays of oscillating energy, e. g. ultra-violet rays, etc., either singly or in combination which are made to irradiate the reaction chamber.

The action in the process of the gases in the presence of which the material is treated during the gas treatment part of the process is intensified by the influence of the rays.

In many cases, it is also advantageous to reduce or to increase the gas pressure during the reaction, for modification of the pressure during

the reaction is generally advantageous. In some cases, I alternately increase and reduce the gas pressure. In others, I alternately use a pressure below and above atmospheric pressure in practicing these processes.

By the process of the present invention, the physical properties of the initial material may be so profoundly modified as to render the end product of the process, after the product has been cooled and stored in the air, or in a gas chamber, a product having entirely new properties. After the reaction, the non-saturated carbon compounds are less active; the iodine number and bromine number are lowered, as is the capacity for chemical reaction and for adsorption.

Although the most favorable concentration and specific action for every cation and/or anion in combination varies for each substance acted upon, any cation and/or anion in combination of the concentration shown in the following examples will operate satisfactorily, provided the electrolyte is soluble in the substance under the applied reaction conditions.

Besides the reacting substances filling materials may be present in every form of treatment.

The modified material produced by my process can be used in a variety of industries, depending upon the properties of the material and the use to which it is to be put. It may be stated, however, that the modified material produced by my process lends itself to use advantageously in the varnish and lacquer industries, in the rubber industry, etc. By my processes I can produce modified materials useful in all the industries which treat artificial substances. Certain products obtained from fatty oils, by my processes, can be used, for instance, in the candle and soap industry as well as in the manufacture of food products, such as artificial fats.

Example I

To 100 grams of linseed oil are added 5 grams of potassium thiocyanate. The mixture is heated in a vacuum for 2 hours at a temperature between 300° and 350° C. At the end of this time, the vacuum is broken and the material is poured into molds and allowed to cool.

Example II

To 100 grams of rape seed oil are added 5 grams of potassium thiocyanate. The mixture is heated in a vacuum for 2 hours at a temperature between 300° and 350° C. At the end of this time, the vacuum is broken and the material is poured into molds and allowed to cool.

In the above examples, 5 grams of cobalt linoleate may be added to the oil in addition to the potassium thiocyanate. Cobalt linoleate serves to further modify the oil products so produced.

Likewise, other salts may be employed in lieu of potassium thiocyanate in the above examples as the primary modifying agent or electrolyte. Various illustrative examples of such salts have been given ante and those containing the anions and cations there indicated are advantageous.

Example III

To 100 grams of linseed oil are added 5 grams of sodium oxalate. The mixture is heated in a vacuum for 2 hours at a temperature between 300° and 350° C. At the end of this time, the vacuum is broken and the material is poured into molds and allowed to cool.

In the above example rape seed oil may be

used in lieu of linseed oil. Also other salts of organic acids may be employed in lieu of sodium oxalate. In other words, Example III is illustrative of the manufacture of modified heat-bodied oils by my processes using a salt of an organic acid as the electrolyte or modifying agent.

The modified, heat-bodied oils obtained in Examples I to III, inclusive, are useful in making varnishes and lacquers. Also they can be treated with sulfur as has been pointed out ante to obtain vulcanized oil products. The manufacture of such vulcanized, modified organic isocolloids is claimed in my application Serial No. 359,425.

Example IV

100 grams of linseed oil, 5 grams of cobalt linoleate and 5 grams of thiocyanate of potash are heated in vacuum for two hours to 300°-350° C. The vacuum is then destroyed, the mass poured into molds and left to cool. The use of the cobalt linoleate as the siccative in addition to the potassium thiocyanate yields a somewhat different product.

Example V

To 100 parts by weight of linseed oil are added 5 parts by weight of sodium bromide, and the mixture is treated in the manner described in Example I. This gives another modified, heat-bodied linseed oil.

This product can be advantageously further treated with sulfur to produce a vulcanized oil product.

In any of the foregoing examples, resins may be substituted for the fatty oils employed in those examples and modified resin products can be obtained.

Example VI

100 grams of mineral cylinder oil and 5 grams of thiocyanate of potassium are heated in vacuum for two hours to 300°-350° C. The vacuum is then destroyed and a modified mineral oil product is obtained.

By adding 5 grams of cobalt linoleate to the above reaction mixture prior to heating, another modified mineral oil product is obtained. With the potassium thiocyanate alone, the modified mineral oil obtained has a viscosity slightly less than that of the original mineral cylinder oil. In the foregoing examples, the reaction may be

effected under pressure, instead of under conditions of reduced pressure, that is, a vacuum as stated therein.

It may also be pointed out that in addition to oils, such as the fatty and mineral oils, shown in these examples, other organic isocolloids, such as resins, etc., may be also modified by these processes.

Of course, I do not limit myself to the exact details described, for obvious modifications may occur to a person skilled in the art. The particular chemicals, amounts, strengths and temperatures mentioned and described herein may be varied without a departure from the scope of my invention as above described and herein-after claimed. That is, the examples given ante are illustrative of my invention and, as suggested, other embodiments may be employed in the practice thereof.

It is well known that by heating fatty oils such as linseed oil etc. to 200° C. or above for several hours, a particular type of bodied oil product is obtained. The bodied oil product so produced are known as "heat-bodied oils", "polymerized oils" or "stand oil", the bodying or polymerization being caused by such heating. The present application is directed to an improvement in such methods, the bodying in such heating being accelerated in the present processes hereinafter claimed.

I claim:

1. In the manufacture of modified heat-bodied oil products from fatty oils, the improved process of enhancing the heat-bodying of the oil which comprises mixing about 5 per cent of dry sodium oxalate with a fatty oil, heating the mixture to temperatures between 300 and 350° C. until said salt is dispersed in said oil and until a substantially solidified, modified, heat-bodied oil product is obtained and then cooling the oil product so obtained.

2. In the manufacture of modified, heat-bodied oil products from fatty oils, the improved process which comprises mixing a minor amount of sodium oxalate with a fatty oil, heating the mixture to temperatures between 300° and 350° C. until said salt is dispersed in said oil and until a substantially thickened, modified, heat-bodied oil product is obtained and then cooling the oil product so obtained.

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