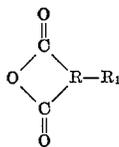


carbon constituent selected from the class consisting of alkyl, alkenyl, aralkyl or aralkenyl groups. The above-described ungelatinized starch acid-esters are prepared by reacting an ungelatinized starch, in an alkaline medium, with a substituted cyclic dicarboxylic acid anhydride having the following formula:



where R and R<sub>1</sub> represent the same substituent groups as are listed above for those same symbols. Substituted cyclic dicarboxylic anhydrides falling within this formula are the substituted succinic and glutaric acid anhydrides.

The starch which is used in making these derivatives may be derived from any source, including corn, wheat, potato, sago, tapioca, waxy maize, rice, sweet potato or arrowroot. It may be in its raw, unmodified state or it may have been previously modified in any desired manner, as for example by hydrolysis, oxidation, dextrinization, esterification or etherification. However, it should be in the ungelatinized form, that is, in the form of its original unbroken granules, and should remain in that form throughout the derivatization process.

As stated, the starch acid-esters are reacted with compounds containing a polyvalent metal ion. Such compounds include, for example, the water soluble salts of aluminum, copper, mercury, zirconium, iron (ferrous or ferric), chromium, tin, calcium, barium, and strontium. Further details for the manufacture of the water-repellent starch derivatives may be found in U.S. Patent 2,613,206, dated October 7, 1952.

The above-mentioned starch derivatives are remarkably resistant to wetting with water. Thus, when the starch derivative in its dry, powdered form is dropped onto water, it tends to remain as a dry mass upon the water's surface. Even after ordinary mixing with the water, it does not form a homogeneous suspension (as would ordinary starch), but rather rises to the top, still dry.

In order to wet the starch derivative so that it may be suspended (and ultimately dispersed) in water, we may employ one of several alternative methods. One method is to moisten it with a water-miscible organic solvent, such as ethanol or methanol. Another method is to moisten the starch with a water-miscible glycol such as glycerol, ethylene or propylene glycol. It may also be moistened with an aqueous ammoniacal solution. Once it has been thus moistened, it has been found that the starch derivative may then be suspended readily in water. Another method is simply to add the starch derivative to water and subject the mixture to high shear stirring, as for example with a "Lightning" mixer, or an Eppenbach stirrer. This high shear stirring, as contrasted to ordinary mixing, tends to beat the starch into the water and cause it to remain in suspension. This latter method has the advantage that it avoids the necessity for the use of organic solvents or other extraneous materials, and also appears to result in a somewhat more water-repellent ultimate encapsulated product.

The first step in the encapsulation procedure is to suspend the starch derivative in water. Methods for accomplishing this have been explained above. The starch, thus suspended in water, is then heated, with agitation, to 180°-200° F., in order to form a uniform, stable dispersion of the starch. The volatile substance to be entrapped (e.g. oil, perfume or the like) is then slowly introduced into the starch dispersion, agitation being continued until emulsification is complete. The emulsion is then dried by any suitable means, such as spray-drying, or spreading on belts and passing through a heating tunnel, or by passing over heated drums. When drying by means other

than spray-drying, it is ordinarily necessary to grind the resultant dried material to the desired particle size.

The resulting encapsulated particles are, in all cases, stable, dry, free-flowing solids which are easily handled by conventional mixing or packaging apparatus without danger of breakage or other damage. When these particles are brought in contact with water, by immersion or moistening, they dissolve very slowly, releasing their entrapped oils or other entrapped substances over an extended period.

With regard to proportions, there are no critical limits. If the previously described starch derivative is employed, it ordinarily requires from about 5 parts to 100 parts or more of the organic solvent, per 100 parts of starch (by weight) in order to moisten it so as to aid its subsequent dispersion in water. If glycerol or one of the other named materials is used as the wetting agent, these proportions may vary somewhat, but it is a matter of the simplest experimentation to determine the optimum quantity. As already stated, it is possible, with proper high shear mixing, to avoid the use of wetting materials entirely.

The aqueous dispersion may have any desired solids content, although we ordinarily employ from about 15% to about 45%, by weight, of the encapsulating agent in the dispersion. The amount of volatile or non-volatile water-insoluble substance which is then emulsified in this dispersion also is subject to variation, depending upon the particular substance being employed. We have emulsified as much as 50% of the substance to be entrapped, based on the weight of the encapsulating agent in the dispersion. All types of oils, perfumes, and other relatively water-insoluble substances are fully compatible with the encapsulating agents.

The following examples will more fully illustrate the embodiment of our invention. All parts are by weight, unless otherwise indicated.

#### EXAMPLE I

This example illustrates the use, as an encapsulating agent, of the water repellent starch derivative comprising the reaction product of aluminum sulfate and an acid converted low viscosity waxy maize acid ester of a substituted succinic acid, derived from octenyl succinic acid anhydride. This product was prepared according to the procedure described in Example IX of U.S. 2,613,206, except that as the starch base we employ a waxy maize starch which had previously been acid converted to a degree known in the trade as 85 fluidity, and the amount of the octenyl succinic acid anhydride used was 3%, based on the weight of the starch.

Five parts of the above described starch derivative were suspended in 20 parts water by high mechanical shear, in an Eppenbach homogenizer. Dispersion (i.e. gelatinization) was effected by heating the mixture with agitation for 15 minutes at a temperature of 185° F. After cooling to 110-120° F., one part of peppermint oil was added to the dispersion and agitation continued until emulsification was complete. This emulsion was then sprayed-dried in a Luwa commercial spray dryer. The input temperature of this device was 420° F. and the output 230° F.

The resulting spray-dried particles were easily handled, relatively free flowing, extremely stable to variations in temperature and relative humidity, and water repellent.

#### EXAMPLE II

This example illustrates the use, as encapsulating agents, of a number of different water repellent starch derivatives. The derivatives employed were as follows:

(1) The reaction product of magnesium sulfate and a low viscosity acid converted corn starch acid ester of a substituted succinic acid (derived from decenyl succinic anhydride). This was prepared according to the procedure of Example I of U.S. 2,613,206, except that