

3

mono-dispersed. Optimum benefits of this invention will not be realized if any substantial portion of the starchy material persists as swollen but undissolved granules or as fragments of such swollen granules. Those versed in the art will be able to judge whether this specification has been met by such means as inspecting the hot cooked starch paste under the phase microscope (when no significant portion of swollen granules or fragments should be visible), or by centrifuging the hot cooked paste (when there should be no substantial precipitate of insoluble material). Under ordinary conditions of cooking, unmodified corn and potato starches do not permit realization of the benefits of this invention, since too much of the total starch substance persists as swollen granules or fragments thereof. Obviously, if any substantial amount of swollen granules or fragments persists, these will be detrimental to the final starchy matrix in two respects: (a) this material will represent material which is not functioning to enclose a dispersed phase in the matrix; and (b) the presence of such discontinuities will weaken the final dried film or matrix, creating fissures which are detrimental to the effectiveness of its protection.

(2) The aqueous starch system must also act as a good suspending agent or protective colloid for the dispersed phase of liquid droplets or of solid particles. Those skilled in the starch art with the aid of simple preliminary tests will readily differentiate between those starch systems which are good protective agents and those which are not. However, in elucidation of this concept of protective colloid action, it is not contemplated, for example, that the dispersed phase shall merely be dispersed through a 5 to 7 percent paste of swollen corn starch granules, i. e., a cooked paste of raw corn starch, since such a dispersion would be maintained primarily by the presence of swollen granules, in contravention of qualification 1 above. Such a system would not produce a film which would enclose and bind the individual particles of the dispersed phase. The ineffectiveness of such a system is illustrated in Example 1, described hereinafter.

(3) The starchy substance should give a stable non-retrograding solution, i. e., it should show little or no tendency to precipitate from solution as insoluble micro-particles. Such retrograded starchy material does not contribute to the starchy matrix and in addition weakens the continuity of this matrix, thus diminishing its protective action. As a criterion of absence of retrogradation, the starchy substance should give a substantially clear solution and should dry down to a flake or film which likewise possesses good clarity. Such a starch will function effectively in this invention, assuming other stipulations are likewise met, as specified herein.

(4) The starchy substance by itself must be one which can be dried down from solution to give a coherent film or flake which is stable and free-flowing, with no tendency either to powder or to form a sticky gum. This quality may be readily established by the simple test of plating out a solution of the starch substance on glass and allowing this film to dry spontaneously at room temperature. It is believed that this property requires that the starchy substance must possess high-polymeric molecular size in order to impart the requisite structural strength and non-hygroscopicity to the film or flake. Thus in Example 1, a partially hydrolyzed corn starch of 16-18 dextrose equivalent gives excellent protection to xanthophyll oil. This same material has an intrinsic viscosity of 0.04 in normal potassium hydroxide solution, and yields a strong red or plum coloration with iodine, which properties may be indicative of a molecular weight of 20-30 glucose units. More important for purposes of defining the starches which are effective in the present invention, this 16-18 D. E. product dries down from solution to give a strong coherent film which is neither powdery nor gummy. In contrast, ordinary 42 D. E. corn syrup dries down to a soft gummy hygroscopic film and hence does not fulfill the stipulated requirement. In addition, corn syrup does

4

not provide adequate protective colloid action as specified above. However, as will subsequently be shown, corn syrup does have usefulness in the present invention as a plasticizer for the primary high-polymeric starchy material.

5. The starchy substance should be soluble in hot water to give solutions of high solids content. The concentrations which have been employed in the practice of this invention have ranged from 0.5-4.0 parts of water per part of starch, depending on the viscosity of the particular starch substance used. While not definitive nor restrictive, the viscosities of the hot cooked starch solutions herein employed have usually been in the region of 15-50 centipoises. More dilute systems can be employed, but some of the useful advantages of this invention will thereby be depreciated. Diluted starch solutions (even where the starchy substance is of a preferred type) do not maintain the dispersed liquid or solid material in stable suspension. Also, there is the added cost of evaporating large quantities of water.

Among the starchy substances which are satisfactory for purposes of this invention are the following general types:

A. The torrefaction or roasted dextrins (variously designated as canary dextrins, yellow dextrins and British gums), which show high solubility in cold water (i. e., usually 80 percent or above), high solution stability (i. e., minimum retrogradation, precipitation and "set-back"), and a very low content of linear starch substance (i. e., as qualitatively indicated by the absence of blue color with iodine; these products usually give red or plum colorations).

B. Thin-boiling oxidized starches, commercially produced by oxidation with hypochlorite or peroxide, especially those having a Scott hot paste viscosity of about 90 to about 45 (on the basis of 100 grams of starch in 280 ml. of water). These starches yield clear stable solutions, with minimal precipitation or "set-back."

C. The etherified starches, including the hydroxyethyl, hydroxypropyl, methyl and ethyl derivatives of low or moderate degree of substitution (D. S. of 0.04 to 0.25 ether groups per glucose unit). In addition, these products should be rendered thin-boiling by acid-modification or oxidation prior to or after derivatization, in order to assist dissolution of granule structure and to permit use of higher starch concentrations. A suitable degree of thinning would correspond to a 5-gram alkali fluidity of about 60 to 90, as measured by the well-known method of Buel (8th Int. Congr. Pure Applied Chem., Orig. Com., 13, 63 (1912)).

D. Starch esters, for example, the slightly acetylated starches described by Cross, Bevan and Traquair (Chem.-Zeit., 29, 527-528 (1905)), or commercially available products described as mixed carboxylic and sulfonic esters of corn starch. To assist dissolution of the granule, the starch esters should be at least moderately thin-boiling, for example, an acetylated starch having a 5-gram alkali fluidity of 56, or a sulfocarboxylic ester marketed under the trade mark of "NuFilm" and having a 5-gram alkali fluidity of 26.

E. Starches which are naturally devoid of a linear fraction, such as waxy maize or waxy sorghum starches. To assist dissolution of the granule and to permit use of higher starch concentrations, these starches should be rendered thin-boiling by appropriate means, e. g., by acid or enzyme hydrolysis, or by oxidation or dextrinization. A minimum degree of such thin-boiling conversion would correspond to a 5-gram alkali fluidity of about 50.

F. Converted starch products within the range of from approximately 4 D. E. to approximately 20 D. E., produced by acidic or enzymic hydrolysis, having high solubility in cold water, the solutions showing good stability against retrogradation, and giving no blue coloration with iodine (suitable products give red to plum colors).

Also, combinations of the above types may be employed, for example, a hydroxyethyl torrefaction dextrin,