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PROCESS FOR COLORING FRUIT

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This invention relates to the treatment of fruit, and more particularly has reference to the coloring of citrus fruit.

Various processes and reagents have been proposed heretofore with respect to the coloring of fruit, but certain objections reside in most of such processes. In general, most of the prior processes have necessitated the use of elevated temperatures, and one of the primary objects of the present invention is to provide a process which may be carried out at such low temperatures that there is no possible danger of injuring the fruit.

In my Patent No. 2,179,762, issued November 14, 1939, I disclosed a process which may be carried out at a temperature of approximately 90° F. The present invention is an improvement over the process there disclosed in several respects. In the first place, the patented process was predicated upon the use of soap as a dispersing or emulsifying agent, whereas my present process obviates the use of soap. Soaps are objectionable in processes of this character. They are alkaline and therefore attack the waxy cuticle of the fruit. The result is that the skin of the fruit is dried out and a very fine pitting is produced. This action of the soap is supplemented, in the patented process, by the water-insoluble solvents that were there specified, namely chlorinated hydrocarbon solvents. The waxy constituents of the cuticle were decidedly soluble in these solvents, and furthermore the solvents were highly volatile and therefore readily lost from the dye bath during actual operation. My present process, in addition to using solvents that are non-deleterious, also uses such relatively small amounts of solvents in the final bath that, even if the solvents were injurious, they would not be present in sufficient amounts to damage the fruit. Moreover the solvents employed are not readily volatile.

Further advantages over Patent 2,179,762 will be apparent from the following description, but, in passing, it should be pointed out that considerably less dye (which is the most expensive item in the bath) is necessary, and further economies result from the fact that a stronger concentrate can be initially made up, thus permitting a greater dilution, and as a consequence the cost of transportation of the concentrate is reduced.

An object of my invention is to provide a process for coloring fruit which may be effectively carried out at such temperatures as will not injure the fruit.

Another object of this invention is to provide a dye bath for citrus fruit in which there are no deleterious constituents, and particularly in which soap and other materials which are substantial wax solvents are excluded.

Yet another object of my invention is to provide a process and bath for the dyeing of citrus fruit which are economical and effective.

To accomplish the above and other objects as will appear more fully hereinafter, my invention in general embraces the concept of a dye bath consisting substantially of water but including an oil-soluble dye dissolved in a suitable solvent and a wetting or dispersing agent. More specifically, the solvent for the dye and the wetting agent are of such chemical compositions, and of such concentrations, that no injury to the fruit results. In the preferred form, the solvent for the dye consists of a water-soluble and/or water-insoluble liquid in which the wax of the orange skin is not soluble to any appreciable extent, and the wetting agent is entirely neutral. In actual practice I have dissolved a relatively small amount of dye in a mixture of a water-soluble solvent such as "Carbitol" the mono-ethyl ether of di-ethylene glycol or "Hexalin" the alicyclic alcohol, cyclohexanol and a water-insoluble solvent for the dye such as glycol dilaurate or dipentene, and have made up a concentrate by adding to such solution a wetting agent of the aryl or alkyl sulfate or sulfonate type, and water. The concentrate so made up can be diluted at the rate of 100 to 300 parts of water to form the actual dye bath.

As mentioned above, one of the objections to the process disclosed in my Patent 2,179,762 resides in the fact that the water-insoluble solvents which I there specify have a tendency to burn the fruit, due to their action upon the wax of the skin, and one of the principal objects of the present invention is the provision of water-insoluble solvents which have no injurious effect. I have found that a number of the hydrocarbons belonging to the alicyclic group, substituted alicyclic group, and aliphatic esters will both dissolve the dye and at the same time will not injure the fruit. Specific compounds which I have used with success have been pinene, dipentene, limonene and glycol dilaurate. It should be pointed out that, while these compounds in concentrated form might cause slight damage of the fruit, I propose using them in such relatively dilute concentrations that no such injury will result.

The water-soluble solvents which may be used in my proposed process may be one of the higher alcohols of the aliphatic group, one of the alicyclic alcohols, one of the chlorhydrins, or one of the glycols or glycol ethers. As instances of the higher aliphatic alcohols that I have used with success are butyl, amyl, hexyl, heptyl and octyl alcohols; as an instance of an alicyclic alcohol there might be mentioned cyclohexanol; ethylene chlorhydrin and propylene chlorhydrin are instances of the chlorhydrins; and, of the

glycols, I have used mono-ethylene glycol and di-ethylene glycol as well as ethers of the same such as sold under the trade-marks "Cellosolve" the mono-ethyl ether of ethylene glycol and "Carbitol" the mono-ethyl ether of di-ethylene glycol.

As mentioned above, soap, being alkaline, has a tendency to dry out the skin of the orange, and the present process contemplates the use of a neutral wetting and dispersing agent which will permit the use of lower temperatures in the dye bath without sacrifice to the coloring of the fruit. I have found that the higher alkyl sulfates, substituted sulfonic acids, and the sulfuric acid derivatives of aliphatic esters are suitable. In each case the compounds that I have used have been the sodium salts of the acids. For instance, I have used a sodium alkyl sulfate sold under the trade-mark "Orvus" (sodium fatty alcohol sulfate); I have used as sodium salts of substituted aromatic sulfonic acids, materials which are sold under the trade-marks "Aromol" (sodium salt of an alkyl benzene sulfonate), "Arylene" (sulfonated aromatic), "NSAE" (alkyl naphthalene sulfonic acid ester), and "Solvadine" (alkylated aryl sulfonate). I have also used a product sold under the trade-mark "Aerosol" as a sulfuric acid derivative of an aliphatic ester as disclosed in Patent No. 2,028,019.

While in the preferred form of my invention I use both a dye solvent that is water-insoluble and a dye solvent that is water-soluble, the process may be practiced by using only a water-insoluble or a water-soluble solvent, but it must be borne in mind that in either event a wetting agent of the class described above must be used. For instance, I have secured entirely satisfactory results by making up a concentrate of the following ingredients, the proportions being by weight.

	Parts
A neutral sodium alkyl sulphate (paste form)	140
Di-ethylene glycol mono-ethyl ether	50
Dye	5
Water	5

It will be noted that the above concentrate omits a water-insoluble solvent for the dye. On the other hand, the water-soluble solvent for the dye may be omitted according to the following formula:

	Parts
A neutral sodium alkyl sulphate (paste form)	140
Pinene	50
Dye	5
Water	5

When desiring both the water-soluble and water-insoluble dye solvents, the following formula may be used:

	Parts
A neutral sodium alkyl sulphate (paste form)	140
Dipentene	25
Cyclohexanol	25
Dye	5
Water	5

The most efficacious wetting and dispersing agents are the sodium salts of substituted aromatic sulphonic acids which appear to have more potent properties than the sodium alkyl sulphates.

Consequently, when using such reagents, the formula may be as follows:

	Parts
A neutral sodium salt of a substituted aromatic sulphonic acid (solid form)	50
Dipentene	25
Cyclohexanol	25
Dye	5
Water	95

The dye which is used in any one of the above mentioned processes will be of the conventional oil-soluble water-insoluble type and must be one of those certified for use in foods—for instance Yellow AB, Yellow OB, FD and C Orange No. 2, or FD and C Red No. 32.

In actually preparing the concentrate, I prefer to use a steam jacketed kettle maintained at a temperature of about 80° C., and in this I first melt the neutral sodium alkyl sulphate and the solvent or solvents. To this mix I add the dye and later the necessary water. In case the wetting agent is in dry form, as for instance with a dry neutral sodium salt of a substituted aromatic sulphonic acid, sufficient water is added to the wetting agent initially to form a liquid and thereafter the solvent or solvents are added. The mixed ingredients are maintained in the kettle until all of the dye goes into complete solution.

The concentrates of my process are so effective that they may be diluted from 1:150 to 1:400, depending upon the exact temperature at which it is desired to actually color the fruit. For warm temperatures of 115° to 120° the dilution may be at the rate of 1:400, while for temperature of the order of 90°, 1:150 would be required.

The bath may be applied to the fruit by dipping the fruit in the bath, by spraying the bath on the fruit, or in any other suitable manner.

Oranges dyed in accordance with the process indicated above will receive a uniform color entirely free of blotching, and of a pleasant, bright and attractive appearance. The dyeing step does not injure the skin of the fruit, even over a long period of time, inasmuch as there are no ingredients in the dye bath which will remove the natural wax of the fruit. It will be observed that the concentrate is so effective that it may be diluted in excess of any dye heretofore available, and this, together with the economy in use of the dye, and particularly the ability to use low temperatures, makes for decided savings in the operation of any packing house.

While I have set forth certain specific ingredients, amounts and steps, it is to be understood that these are exemplary merely, and that the scope of my invention is to be determined solely by the breadth of the appended claims.

I claim:

1. In a process of coloring citrus fruits the steps comprising preparing a neutral dye concentrate comprising a water-insoluble, oil-soluble dye, a neutral dye dispersing agent, a water soluble organic dye solvent, a low volatile water insoluble organic dye solvent and water, each of said dye solvents being characterized by the insolubility of natural fruit wax therein, dispersing a minor proportion of said dye concentrate in an aqueous medium to form a stable neutral aqueous dispersion of said concentrate and thereafter contacting citrus fruits with said aqueous dispersion to color the fruit without removing the natural wax content thereof.

2. In a process of coloring citrus fruits, the steps comprising preparing a neutral dye concentrate comprising a water-insoluble, oil-soluble

dye, a neutral dye dispersing agent, a water-soluble organic dye solvent, a water-insoluble organic dye solvent selected from the group consisting of pinene, dipentene, limonene and glycol dilaurate, and water, each of said dye solvents being characterized by the insolubility of natural fruit wax therein, dispersing a minor proportion of said dye concentrate in an aqueous medium to form a neutral aqueous dispersion of said concentrate, and thereafter contacting citrus fruits with said aqueous dispersion to color the fruit without removing the natural wax content thereof.

3. In a process of coloring citrus fruits, the steps comprising preparing a neutral dye concentrate comprising a water-insoluble, oil-soluble dye, a neutral dye dispersing agent, a water soluble organic dye solvent selected from the group consisting of higher aliphatic alcohols, alicyclic alcohols, chlorhydrins and glycols, a water-insoluble organic dye solvent selected from the group consisting of pinene, dipentene, limonene and glycol dilaurate, and water, each of said dye solvents being characterized by the insolubility of natural fruit waxes therein, dispersing a minor proportion of said dye concentrate in an aqueous medium to form a neutral aqueous dispersion of said concentrate, and thereafter contacting citrus fruits with said aqueous dispersion to color the fruit without removing the natural wax content thereof.

4. In a process of coloring citrus fruits, the steps comprising preparing a neutral dye concentrate comprising a water-insoluble, oil-soluble dye, a neutral dye dispersing agent, a water-insoluble organic dye solvent selected from the group consisting of pinene, dipentene, limonene and glycol dilaurate, and water, each of said dye solvents being characterized by the insolubility of natural fruit waxes therein, dispersing a minor proportion of said dye concentrate in an aqueous medium to form a neutral aqueous dispersion of said concentrate, and thereafter contacting citrus fruits with said aqueous dispersion to color the fruit without removing the natural wax content thereof.

5. In a process of coloring citrus fruits, as set forth in claim 3 wherein the proportion of the dye concentrate to aqueous medium is from 1:400 to 1:150.

6. In a process of coloring citrus fruits as set forth in claim 4, wherein the proportion of dye concentrate to aqueous medium is from 1:400 to 1:150.

7. In a process of coloring citrus fruits, the steps comprising preparing a neutral dye concentrate comprising five parts of a water-insoluble, oil-soluble dye, one hundred forty parts of a neutral dye dispersing agent, fifty parts of pinene a water insoluble organic dye solvent characterized by the insolubility of natural fruit waxes therein, and five parts of water, dispersing one part of said dye concentrate in from four hundred to one hundred fifty parts of an aqueous medium to form a neutral aqueous dispersion of said dye concentrate, contacting citrus fruits with said aqueous dispersion to color the fruit without removing the natural wax content thereof.

8. In a process of coloring citrus fruits, the steps comprising preparing a neutral dye concentrate comprising five parts of a water-insoluble, oil-soluble dye, from fifty to one hundred forty parts of a neutral dye dispersing agent, twenty-five parts of cyclohexanol, twenty-five parts of dipentene, and five parts of water, dispersing one part of said dye concentrate in from four hundred to one hundred fifty parts of an aqueous medium to form a neutral aqueous dispersion of said dye concentrate and thereafter contacting citrus fruits with said aqueous dispersion to color the fruit without removing the natural wax content thereof.

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