

## UNITED STATES PATENT OFFICE

20,490

METHOD OF REMOVING SPRAY RESIDUE  
FROM FRUIT

Harry C. McLean and Albert L. Weber, New Brunswick, N. J., assignors to Endowment Foundation, New Brunswick, N. J., a corporation of New Jersey

No Drawing. Original No. 2,003,005, dated May 28, 1935, Serial No. 695,505, October 27, 1933. Application for reissue August 1, 1935, Serial No. 34,224

18 Claims. (Cl. 99—103)

This invention relates to the washing of fruits and vegetables, such as apples, pears, string beans, peas, lettuce and the like to remove spray materials from the surface thereof.

5 More particularly, the present invention is directed to the removal of arsenic or lead compounds which may be associated with mineral oils and which have been used in various combinations for spraying fruit trees to eradicate  
10 certain insect pests. The invention is also applicable to waxy fruit and the like in which the spray residues have become embedded in the wax, and which may not have been oil sprayed. Recently the Government has lowered the toler-  
15 ance on the content of both arsenic and lead on fruit for edible purposes so that it has become increasingly essential that a washing operation be conducted to effectively remove these materials. Where a mineral oil has been used for  
20 spraying purposes it may stimulate the formation of a resistant waxy covering on the fruit which prevents the ready access of the washing solution and thus tends to prevent effective cleaning of the fruit and removal of the lead and  
25 arsenic.

A number of methods for washing sprayed fruit have been developed and used. These have been only indifferently successful and have not  
30 always served to bring the arsenic and lead content down below the relatively small amount allowed by the Government. One of these processes consisted in providing a solution of hydrochloric acid with an emulsion of kerosene. The solution was heated to about 100° F. and the  
35 fruit washed therein. This process was unable to remove the arsenical residue sufficiently from fruit sprayed with mineral oil, fish oil, or fish oil soaps, and lead arsenate to meet the export or the domestic market requirements.

40 Another previously proposed process consisted in first dipping the fruit in methyl alcohol solution to remove the coatings of oil or wax which form on the fruit, after which the fruit was subjected to a cleaning operation with hydrochloric  
45 acid solution. This process offered serious difficulties in that it was necessary to conduct two separate washing operations which greatly increased the cost of processing because of the need for maintaining additional washing equipment.  
50 The methyl alcohol may have detrimental effects on the health of the workers which is caused by prolonged exposure to the alcoholic vapors.

Still another process of the prior art resided in the use of such detergents as trisodium phosphate, sodium carbonate or sodium silicate in

solution for washing fruit and the like. These substances do not remove the lead from the fruit to a satisfactory degree in all cases, and the solutions must be heated, say to 90°–100° F., in order to make them at all effective.

The present invention is directed to the washing of fruit with a solution which is comparatively inexpensive and which is capable of effectively removing the arsenical and lead residues from lead arsenate and oil sprayed fruit.

10 It is among the objects of our invention to provide a solution for washing fruit which is non-inflammable in nature, which in no way detrimentally affects the keeping qualities or appearance of the fruit, which has a sufficiently high  
15 solvent action so that without the necessity of applying heat it will remove the undesirable residues from the fruit, which will in no way endanger the health of the workers, and which is suitable for use with either the homemade flotation washers and dipping tanks, or for use with  
20 the various types of commercial washing machines in which a short period of contact between the fruit and the washing solution is maintained.

25 In practicing our invention, we provide a water solution of an acid, preferably a mineral acid, such as hydrochloric, nitric or the like, although for practical purposes hydrochloric acid has been found extremely well suited. The amount of hydrochloric acid in solution is generally not over  
30 three percent and usually is from 1 to 2 percent by weight. In some cases up to 5% of the HCl may be used. To this solution, we add a degumming or wetting agent of the type which is made by the sulphonation of the higher aliphatic alcohols, higher fatty acids and the higher aliphatic and aromatic hydrocarbons, said compounds containing at least six carbon atoms.  
35 Usually the sulphonic compound, which is termed a sulphonic acid, is neutralized so as to form an alkali metal salt thereof. The preparation of such substances is well known and need not be here described.

40 While we are enabled to use substantially all of the degumming agents of the above described types, we have found that a sulphonated naphthalene compound such as the alkylated naphthalene sulphonic acids or their alkali metal salts are well adapted for our purpose. Among  
45 such compounds, we have specifically tested the sodium salts of the butyl and propyl naphthalene sulphonic acids, as well as the sodium salt of abietene sulphonic acid. We have found that in  
50 conjunction with the degumming agent, if there  
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is present a substantial proportion of a water soluble salt such as, sodium chloride, or sodium sulphate, increased effectiveness in the resultant operation is obtained.

5 A solution of the above described type is very effective in the removal of the arsenical residue, but we have found that in washing apparatus having positive agitation, considerable foaming takes place which may result in over-flowing of  
10 the froth from the apparatus and thus result in the loss of washing solution. To overcome this, we generally add to the solution a substance which is adapted to prevent the foaming. While a considerable number of substances of various types  
15 may be used for this purpose we find that substances taken from the following class, aliphatic ketones and alcohols having from 6 to 10 carbon atoms, pine oil, fusel oil, degreas, naphtha or mixtures thereof, usually in comparatively small  
20 amounts, produce the desired anti-foaming effects.

The washing solutions may vary greatly in the composition thereof. As indicated above, the amount of hydrochloric acid should ordinarily  
25 be not over three percent and is usually from 1 to 2 percent by weight. The amount of the degumming agent is usually not over 2 percent and ordinarily from  $\frac{1}{2}$  to 1 percent or even less, has been found suitable for the purpose. When a  
30 soluble salt is used in conjunction with the degumming agent, it is not necessary to use more than about 1 to 2 percent thereof. A considerably smaller proportion of anti-foaming substance is required and ordinarily we use not over  
35 .5% thereof, and in most cases from .1 to .2 percent was sufficient to prevent foaming.

The washing operation with the use of a degumming or wetting agent in the solution is ordinarily conducted at normal atmospheric temperatures,  
40 say for example about 70° F. In most cases it is unnecessary to heat the solutions, which was considered essential in prior processes. The washing operation may be conducted for any desired length of time such as is usual in fruit  
45 washing. For instance, in the spray and flood type of washing machines the fruit may be held in contact with the acid solution for about  $\frac{1}{2}$  to 1 minute. In the commercial type of washer heating to 100° F. for a short time assists in the  
50 removal of spray residues in a shorter time but heating is not at all essential. With the home-made flotation type of washing machine the period of contact may be on the average about 3 minutes followed by thorough rinsing in water.  
55 Repeated tests on fruit which had been subjected to this process, and which had been safely sprayed with lead arsenate and calcium caseinate or with lead arsenate and petroleum oil, have shown that the rated capacity of the washing  
60 machines is very materially increased by the use of a degumming or wetting agent as disclosed herein, due to the rapid and effective contact established between the hydrochloric acid and the lead arsenate. This is probably due to the rapid  
65 removal from the surface of the fruit of the oil or the outer film of the wax in which the spray residues are embedded, allowing the hydrochloric acid to make direct contact with the lead arsenate and dissolve the same. By the use of this inven-  
70 tion, the washed fruit shows no deleterious effects after long storage and the surface of the fruit is bright and clear.

Although we have described our invention setting forth the general nature thereof and indicating the various materials and proportions

which have been found adapted for commercial practice, it is to be understood that our invention is not limited to the details described herein. It will be apparent to those skilled in the art that variations in the strength of solutions, in the time of contact of the fruit with the solutions, and the type and character of the apparatus used for washing, may be made at will with good results. The character and the amount of spray, as well as the length of storage of the fruit prior to the washing operation, may necessitate wide variations in the composition of the washing solutions and in the times of treatment. These and other changes are considered to be within the scope of this invention which is not to be limited except by the claims appended hereto.

We claim:

1. A method of washing fruit and the like to remove spray materials from the surface thereof which includes applying to the fruit a solution containing a small proportion of hydrochloric acid and an alkali metal salt of a sulphonated hydrocarbon.

2. A method of washing fruit and the like to remove spray material from the surface thereof which includes applying to the fruit a solution containing a small proportion of hydrochloric acid and a sulphonated aromatic hydrocarbon.

3. A method of washing fruit and the like to remove spray material from the surface thereof which includes applying to the fruit a solution containing a small proportion of hydrochloric acid and a sulphonated substituted aromatic hydrocarbon.

4. A method of washing fruit and the like to remove spray material from the surface thereof which includes applying to the fruit a solution containing a small proportion of hydrochloric acid and a sulphonated naphthalene.

5. A method of washing fruit and the like to remove spray material from the surface thereof which includes applying to the fruit a solution containing a small proportion of hydrochloric acid and a sulphonated alkylated naphthalene.

6. A method of washing fruit and the like to remove spray material from the surface thereof which includes applying to the fruit a solution containing a small proportion of hydrochloric acid, a sulphonated aromatic hydrocarbon and a soluble salt.

7. A method of washing fruit and the like, to remove spray material from the surface thereof which includes applying to the fruit a solution containing a small proportion of hydrochloric acid, a sulphonated aromatic hydrocarbon and sodium chloride.

8. A method of washing fruit and the like to remove spray material from the surface thereof which includes applying to the fruit a solution containing a small proportion of hydrochloric acid, a sulphonated aromatic hydrocarbon and a substance adapted to prevent foaming of the solution.

9. A method of washing fruit and the like, to remove spray material from the surface thereof which includes applying to the fruit a solution containing a small proportion of hydrochloric acid, a sulphonated aromatic hydrocarbon and a substance adapted to prevent foaming of the solution taken from the following class consisting of:—aliphatic ketones and alcohols having from 6 to 10 carbon atoms, pine oil, fusel oil, degreas, naphtha.

10. A method of washing fruit and the like to remove spray materials from the surface thereof

which includes applying to the fruit a solution containing not over 3% of hydrochloric acid by weight and a smaller amount of a sulphonated aromatic hydrocarbon.

- 5 11. A method of washing fruit and the like to remove spray material from the surface thereof which includes applying to the fruit a solution containing about 1.0-2.0 percent of hydrochloric acid by weight and about 0.50-2.0 percent of a  
10 soluble salt by weight and about 0.50-1.0 percent of a sulphonated aromatic hydrocarbon.

12. A method of washing fruit and the like to remove spray materials from the surface thereof which includes applying to the fruit a solution  
15 containing about 1.0-2.0 percent of hydrochloric acid by weight and about 0.50-1.0 percent of a sulphonated alkylated naphthalene.

13. A method of washing fruit and the like to remove spray material from the surface thereof  
20 which includes applying to the fruit a solution containing about 1.0-2.0 percent of hydrochloric acid by weight, about 0.50-1.0 percent of a sulphonated aromatic hydrocarbon and not over 0.5 percent of a substance adapted to prevent  
25 foaming of the solution.

14. A method of washing fruit and the like to remove spray material from the surface thereof which includes applying to the fruit a solution containing a small proportion of hydrochloric  
30 acid and a sulphonated organic compound taken from the following class consisting of:—higher

aliphatic alcohols, higher fatty acids, higher aliphatic and aromatic hydrocarbons.

15. A method of washing fruit and the like to remove spray material from the surface thereof which includes applying to the fruit a solution containing a small proportion of hydrochloric acid and a sulphonated organic compound taken from the following class consisting of:—higher aliphatic alcohols, higher fatty acids, higher aliphatic and aromatic hydrocarbons in the form of their alkali metal salts.  
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16. A method of treating fruit and the like to remove spray materials from the surface thereof which includes washing the fruit and the like with a solution comprising an alkali metal salt of a sulphonated hydrocarbon, hydrochloric acid and water, and then rinsing with water.  
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17. A method of washing fruit and the like to remove spray materials from the surface thereof which includes applying to the fruit a solution containing a small proportion of hydrochloric acid and an alkali metal salt of a sulphonated aromatic compound.  
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18. A method of washing fruit and the like to remove spray materials from the surface thereof which includes applying to the fruit a solution containing a small proportion of hydrochloric acid and an alkali metal salt of a sulphuric ester of a higher aliphatic alcohol.  
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HARRY C. McLEAN.  
ALBERT L. WEBER.  
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