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SUPPRESSION OF EVAPORATION OF HYDROCARBON LIQUIDS

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17 Claims. (Cl. 21—60.5)

This invention relates to a method and a means for reducing the rate of evaporation of stored hydrocarbon liquids. It relates particularly to a method and a means for reducing the rate of evaporation of stored hydrocarbon liquids having a free surface within a storage container, and having further a multiplicity of discrete, relatively small particles floating on this surface.

Fairly recently the practice has come into use of providing non-rigid, continuous coverings comprising some thicknesses of plastic, hollow, spherical particles of exceedingly small size on the surfaces of hydrocarbon liquids in storage vessels to reduce evaporation losses of these liquids. These particles are of low density and float on the liquid surface. A species of such particles comprises nitrogen-filled microspheres of thermo-setting plastic. They may be made from phenol-formaldehyde resin or other oil-insoluble resins, polyethylene, etc., according to the process disclosed in U.S. Patent No. 2,797,201, issued to F. Veatch and R. W. Burhans on June 25, 1957. Their use as liquid surface coverings is exemplified in U.S. Patent No. 2,797,138 to F. Veatch and E. C. Hughes, and U.S. Patents Nos. 2,797,139, 2,797,140 and 2,797,141 to F. Veatch, all issued on June 25, 1957. These microspheres may have an average diameter of 1 to about 500 microns, preferably 25 to 250 microns. Their bulk density is within the range of 0.01 to 0.3, preferably 0.1 to 0.2, and liquid displacement density within the range 0.05 to 0.6, preferably 0.2 to 0.5.

The liquid surface covering of hollow, floating-microspheres, also called "microballoons," may have a thickness of about 0.4 to 4.0 inches. The preferred thickness varies according to the type of service. For example, in a tank for storing a petroleum naphtha such as aviation turbo-jet fuel of grade JP–4, surface coverings of thicknesses between 1.0 and 1.5 inches have been used. This particular usage of microspheres will be discussed subsequently herein. For another example, in a tank into and from which petroleum crude oil is pumped continuously or at frequent intervals, as in the so-called working tanks used in connection with a pipeline that transports crude oil, the preferred thickness of the surface covering is about one-half inch. In any application, however, the liquid surface covering will comprise many superimposed layers of microspheres. It will have a substantially continuous contact with the liquid surface on which it rests. Likewise it will flow laterally to make an effectively continuous peripheral contact with the walls of the vessel in which the liquid is being stored or transported.

It is, however, characteristic of conventional microspheres consisting essentially of materials of the nature mentioned above that they will be "wetted" by hydrocarbon liquids whereon they float. In view of the individually small sizes of the microspheres, and the plurality of points of contact that any single microsphere will have with those around it to create a multiplicity of tiny passages through the microsphere covering on the liquid, this wetting effect will produce a capillary or "wicking" action. This action causes hydrocarbon liquid to rise through the many tiny passages between the microspheres. The liquid thus reaches the top surface of the microsphere covering, and negates its effectiveness as a blanket to seal the hydrocarbon liquid from the vapor zone of the storage vessel.

Despite this capillary action which causes transport of hydrocarbon liquid to the top of the microsphere covering, microspheres have been effective in the reduction of evaporation from heavier hydrocarbons such as petroleum gas oil and crude oil. In these instances, capillary action proceeds as previously described. However, after some evaporation of the transported liquid has taken place from the top of the microsphere covering, a very heavy pitch-like residue is formed at this level which then becomes relatively impermeable to vapor passage.

The situation is different in the case of light hydrocarbons, however, since no heavy hydrocarbon component is present and no pitch-like residue is formed. Therefore, capillary feeding through the microsphere covering on and subsequent vapor losses from such liquids proceed continuously. Laboratory tests and field trials of these microspheres have demonstrated their relative ineffectiveness in suppressing evaporation of light hydrocarbon products such as petroleum naphtha mentioned above because of this capillary action. Greater thicknesses of the microsphere covering have been employed in an effort to overcome this action in the cases of the lighter hydrocarbons with little or no beneficial effect. In fact, it has been demonstrated that ordinary microspheres may even accelerate evaporation of light hydrocarbon liquids as will be shown subsequently.

According to this invention, a non-wettable agent is applied as a coating or surficant onto the microspheres. This prevents them from becoming wet by the liquid and hence it is impossible for capillary action to proceed. The evaporation of hydrocarbons is thus suppressed by a covering in the nature of a plurality of individually buoyant objects which cannot be wetted by the liquid (either hydrocarbon or water). In keeping with the principles already stated, this non-wettable treatment of the particles comprising this covering makes them effective as an evaporation suppressant for all types of hydrocarbon liquids.

There are several materials that can be applied to microspheres of the general type already described to produce this non-wettable property. Compounds belonging to the silicone family and also those belonging to the fluorcarbon (fluorinated hydrocarbon) family can be employed. These materials are insoluble in oil, and hence are not dissolved from the microspheres. They demonstate excellent tenacity as a coating on the microspheres in much the same manner as a paint film. The microspheres, when coated with materials of these types, cannot be wetted by water or any grade of hydrocarbon.

These non-wettable surficants, i.e., silicones, fluorocarbons, are deposited as films on the microspheres by simple spraying while the microspheres are in gentle motion, for example, spraying the microspheres in a tumbling barrel to insure uniformity of deposition. As an alternate, dipping of the microspheres into a bath of the non-wettable agent may be employed. Again gentle motion is desirable to insure uniform drying and prevent agglomeration of the particles. In the case of the fluorcarbon material, a coating thickness such as to comprise 1.5 wt. percent to 6.0 wt. percent, preferably about 2.0 wt. percent, of the microsphere as previously formed has been found to give satisfactory results.

When microspheres are treated in this manner with a non-wettable surficant and thereafter used as covering for light hydrocarbon liquids, the effectiveness of this invention has been clearly demonstrated by extensive laboratory tests. In one instance, a 1.0 inch thick covering of untreated microspheres was placed on the surface of 1,530 milliliters of petroleum naphtha contained in a 2,000-milliliter beaker. A similar covering comprising microspheres of the same size and of the same lot that were coated with a non-wettable surficant of the fluorcarbon family according to this invention was placed over the same quantity of petroleum naphtha in a second 2,000-milliliter beaker. A third 2,000-milliliter beaker was simply filled with 1,530 milliliters of petroleum naphtha to be employed as a control or datum. The test was conducted at room temperature, 72° F., and stagnant air conditions. The top surface area of the hydrocarbon liquid was 19.6 square inches in each beaker. The evaporation loss results are summarized in the following table:

Table

Exposure Time, Hrs.	Percent Loss from Beaker		
	Petroleum Naphtha with treated Microsphere covering	Petroleum Naphtha with untreated Microsphere covering	Petroleum Naphtha with no covering (Control)
0	0	0	0
21	7.5	35.0	42.5
93	20.0	90.0	68.5
117	25.0	100	72.5
165	32.5		80
261	45.0		100
357	55.0		

After a 117-hour exposure period, the untreated microsphere beaker had an evaporation loss of 1,530 milliliters (100%) and the control beaker of naphtha had an evaporation loss of 1,110 milliliters (72.5%). It will be noted that the ordinary microspheres actually accelerated evaporation during the first 117-hour interval. On the other hand, the beaker with the microspheres treated with a non-wettable surficant according to this invention lost only 383 milliliters (25.0%) during the initial 117 hours, clearly demonstrating the effectiveness of such treatment to prevent wetting of microspheres and subsequent capillary action.

In general, a closely packed microsphere covering is desirable in respect of suppression of evaporation losses. Such close packing may, however, be obtained by the use of at least some spherical particles of diameters lying beyond the 1 to 500-micron range previously cited. By the use of covering particles of a fairly wide range of sizes—i.e., 0.5 inch and somewhat smaller diameter particles with others much smaller such as those of 25 to 250-micron diameter, a covering may be obtained that will be equally as effective as the complete smaller particle covering since the large interstices between the large (0.5 inch diameter) particles will be filled with the smaller particles (25 to 250 microns).

An advantage of using substantially spherical covering particles is that they are suitable for easy handling by pumps and by mechanical foam-eductors, as is well known in the art. A slight disadvantage is that perfect spheres make only point contacts with one another. However, in a covering made up to a thickness of 0.5 inch with microspheres having diameters less than 500 microns, each sphere is in contact with several other spheres around it and a sufficient number of point contacts always exists to insure that a closely packed covering results. Nevertheless, non-spherical buoyant bodies of irregular or regular dimensions and with either smooth or roughened external surfaces that have been treated with a non-wettable surficant may be used in accordance with this invention also.

What is claimed is:

1. A vessel characterized by wall elements, a hydrocarbon liquid body partially filling said vessel and having a free surface therein, and a covering means on said liquid surface which comprises a plurality of discrete particles having an average diameter in the range of 1 micron to 0.5 inch, said particles being in continuous rubbing contact with each other and with said wall elements, and

being individually characterized by a superimposed exterior surface film which is essentially non-wettable by said hydrocarbon liquid; said film constituting from 1.5 to 6.0 wt. percent of said particle.

2. A vessel characterized by wall elements, a hydrocarbon liquid body partially filling said vessel and having a free surface therein, and a covering means on said liquid surface according to claim 1, said covering means having a thickness in the range 0.4 to 4.0 inches.

3. A vessel characterized by wall elements, a hydrocarbon liquid body partially filling said vessel and having a free surface therein, and a covering means on said liquid surface according to claim 1, said covering means having a thickness in the range 1.0 to 1.5 inches.

4. A vessel characterized by wall elements, a hydrocarbon liquid body partially filling said vessel and having a free surface therein, and a covering means on said liquid surface according to claim 1 in which said particles are of essentially spherical configuration.

5. A vessel characterized by wall elements, a hydrocarbon liquid body partially filling said vessel and having a free surface therein, and a covering means on said liquid surface according to claim 4 in which said particles have an average diameter not greater than 0.5 inch.

6. A vessel characterized by wall elements, a hydrocarbon liquid body partially filling said vessel and having a free surface therein, and a covering means on said liquid surface according to claim 4 in which said particles have an average diameter in the range 1 to 500 microns.

7. A vessel characterized by wall elements, a hydrocarbon liquid body partially filling said vessel and having a free surface therein, and a covering means on said liquid surface according to claim 4 in which said particles have an average diameter in the range 25 to 250 microns.

8. A vessel according to claim 1, wherein said particles are essentially hollow, spherical and gas filled.

9. A vessel according to claim 8, wherein said exterior surface film is a silicone compound.

10. A method of reducing the rate of evaporation from the free surface of a body of liquid which comprises covering said liquid surface with a plurality of discrete particles in continuous rubbing contact with each other, said particles having an average diameter in the range one micron to one-half inch, each being essentially hollow, spherical, and gas filled, and having a continuous exterior surface film of a material essentially non-wettable by said liquid; said film constituting from 1.5 to 6.0 wt. percent of said particle.

11. A method according to claim 10, wherein the quantum of said particles is sufficient to provide a covering thickness in the range of 0.4 to 4.0 inches.

12. A method according to claim 10, wherein the quantum of said particles is sufficient to provide a covering thickness in the range of 1.0 to 1.5 inches.

13. A method according to claim 10, wherein said particles have an average diameter not greater than 500 microns.

14. A method according to claim 24, wherein said particles have an average diameter in the range of 25 to 250 microns.

15. A method according to claim 10, wherein said exterior surface film consists essentially of a silicone compound.

16. A vessel characterized by wall elements, a hydrocarbon liquid body partially filling said vessel and having a free surface therein, and a covering means on said liquid surface which comprises a plurality of discrete essentially hollow spherical and gas-filled particles having an average diameter in the range of 1 micron to 0.5 inch, said particles being in continuous rubbing contact with each other and with said wall element, and being individually characterized by a superimposed exterior surface film which is a fluorocarbon compound; said film constituting from 1.5 to 6.0 wt. percent of said particle.

17. A method of reducing the rate of evaporation from the free surface of a body of liquid which comprises covering said liquid surface and a plurality of discrete particles in continuous rubbing contact with each other, said particles having an average diameter in the range of one micron to one-half inch, each being essentially hollow, spherical and gas-filled, and having a continuous exterior surface film consisting essentially of a fluorocarbon compound; said film constituting from 1.5 to 6.0 wt. percent of said particle.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,146,060 August 25, 1964

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 38, for "spheres, also called "microballoons," may" read -- spheres may --.

Signed and sealed this 6th day of April 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents