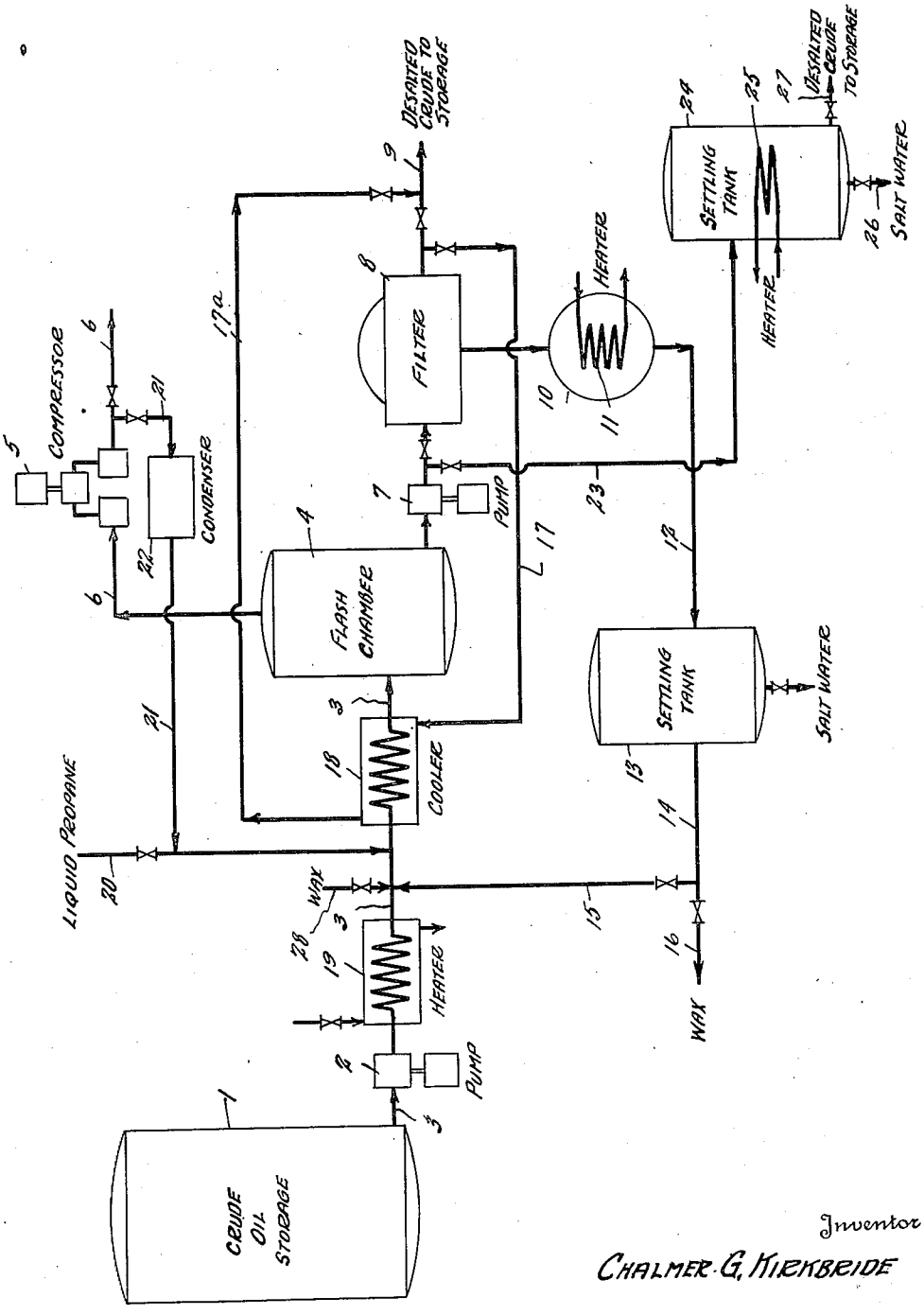
Jan. 9, 1945. C. G. KIRKBRIDE 2,366,792

DESALTING OF MINERAL OIL

Filed May 27, 1942



Inventor

CHALMER G. KIRKBRIDE

By Semmes, Keegin, Beale & Semmes

Attorneys

Patented Jan. 9, 1945

2,366,792

UNITED STATES PATENT OFFICE

2,366,792

DESALTING OF MINERAL OIL

Chalmer G. Kirkbride, Texas City, Tex., assignor to Pan American Refining Corporation, Texas City, Tex., a corporation of Delaware

Application May 27, 1942, Serial No. 444,711

13 Claims. (Cl. 252—348)

This invention relates in general to the desalting of mineral oil and more particularly has reference to the separation of salt in the form of a wax-salt water mixture by subjecting the oil to dewaxing procedures.

Crude oil contains salt in varying degrees, depending on the field and the nature of the strata from which the crude is obtained. The salt content may vary from zero to values as high as 100 grams per barrel or even higher, for example, the amount of salt in East Texas may vary from about 15 to 20 grams per barrel, whereas for Cayuga crude the salt content may be about 80 grams per barrel or higher. The variation in salt content will also depend on the season of the year, the salt content being higher during the winter season when it is more difficult to separate the salt water from the crude. This salt or salt water in the crude is the cause of corrosion and also fouling of heat exchangers, furnace tubes, and parts of the distillation equipment. Also in the case of catalytic cracking, it has a detrimental effect on catalyst activity and life. It is, therefore, apparent that the salt in crude oil is an objectionable impurity and many procedures have been developed for its removal. Fortunately, it is not necessary to completely remove the salt inasmuch as salt contents as low as 2 grams to 3 grams per barrel usually will not cause significant damage to the catalyst or fouling of heat exchangers, furnace tubes, etc.

Salt in crude oil is an objectionable impurity and many procedures for its removal have been developed. While some of these procedures are effective they involve extensive manipulations and add to the cost of the products to be made from the crude oil.

Wax is another undesirable impurity present in various proportions in crude oils from various sources and many procedures have been proposed for effecting the dewaxing of such oils. In most instances the dewaxing is not effected from the crude oil but from partially refined oil and after desalting.

A major object of this invention is the desalting of crude oil.

Another object of this invention is to effect simultaneous desalting and dewaxing of crude oil.

A further object of this invention is to provide a method of desalting crude oil by precipitating existing or added wax in the form of separable wax-salt water mixtures and separating the precipitated material from the oil.

Still another object of this invention is to provide a method of desalting crude oil by heating the oil to above atmospheric temperature, adding wax thereto, cooling the oil to atmospheric temperature to effect precipitation of the wax together with salt water admixed therewith and separating the precipitated mixture.

A still further object of this invention is to provide a method of desalting crude oil by precipitating existing or added wax in the form of separable wax-salt water mixtures, separating the wax from the salt, and recovering the separated wax for further use in desalting.

Yet another object of this invention is to provide a method of desalting crude oil by precipitating existing or added wax in the form of separable wax-salt water mixtures by cooling the oil by expanding contained or added liquefied light hydrocarbon fractions and separating the precipitated material from the oil.

With these and other objects in view which will appear hereinafter, the invention embodies generally the steps of separating existing or added wax along with the salt from salt containing crude oil by cooling the oil to a temperature at which the wax-salt water mixture or emulsion will precipitate and then separating the mixture or emulsion from the oil.

In order to facilitate an understanding of this invention, reference is made to the accompanying drawing in which the single figure illustrates diagrammatically a system for carrying out the present invention.

It has been found that when a crude oil containing wax crystals is allowed to stand, the wax crystals will settle and the bottom layer formed principally of wax will also have a very much higher salt content than the remaining portion of the oil. For instance, in the case of East Texas crude oil, the salt content of the wax layer obtained after standing might be as high as 3000 to 5000 grams per barrel. On the other hand, in crude oils not having a high wax content such as those obtained from Hastings and South Houston, the salt water remains to a large extent in the form of an emulsion and mere settling may not greatly reduce the salt content of the oil.

It is believed that the settling of the wax crystals entrains small droplets of salt water to form a mixture or emulsion and when the wax crystals settle the salt water is carried along with the wax, thereby reducing the salt content of the crude oil. The salt particles or salt water particles may act as nuclei for the crystallization of wax such that when the wax is crystallized, the greater proportion of the salt water nuclei are

entrained during the precipitation of a relatively small portion of the total wax content of the crude oil. It has been ascertained by microscopic examinations that the wax crystals settled from the oil actually enmesh the salt water particles. In one particular instance it was found that crude oil containing about 40 grams of salt per barrel had its salt content reduced by the separation of the wax therefrom to about 0.

In the case of crude oils having a low wax content such as those obtained from Hastings and South Houston, the salt water content can still be removed in accordance with the present invention by adding crystalline wax to the crude, thereby increasing its wax content to such a point that when crystallization is effected, sufficient salt solution will be entrained in the wax crystals to effect the removal of a considerable portion of the salt water solution content.

In the case of crude oils having a small wax content and in which it would be impractical to cool to a sufficiently low temperature to precipitate the wax, the crude oil is heated to a temperature somewhat higher than atmospheric, and preferably to a temperature sufficient to place the wax in true solution, usually 125° to 140° F. Under these conditions the pressure should be maintained sufficiently high that the desired volatile constituents of the crude oil will not be distilled off. After heating to the proper temperature, the required amount of wax is added to the crude so that a portion of this wax will be precipitated at the desired settling temperature. Ordinarily a crystalline type of wax should be added to the oil, although in some cases it may be desirable to add an amorphous wax. The wax which is added should be preferably of relatively high melting point in order to facilitate its precipitation without necessitating extremely low cooling temperatures. If the amount of added wax is sufficiently high in quantity and has a high melting point, it is possible to effect the desired crystallization by merely cooling to atmospheric temperature and avoiding the necessity of refrigeration equipment. However, in order to avoid the necessity of adding extremely large quantities of wax, some form of moderate refrigeration, for example, cooling to 50° F. which can be easily and economically effected with vacuum jet refrigeration equipment, is advantageously adopted. Following the addition of the proper quantity and kind of wax, the crude oil is then cooled to atmospheric temperature or lower if necessary and the wax which was placed in solution at the higher temperature will then be precipitated and during the precipitation will entrain the salt water and thereby effectively desalt the crude. The mixture or emulsion of wax and salt water may be removed either by settling and decantation or by filtration.

In cooling the crude oil to effect precipitation of the wax and the entrained salt water, various refrigeration means may be employed. It is also within the concept of the present invention to effect internal refrigeration of the crude oil by evaporation of a portion of the crude oil itself, that is, evaporation of some of its lighter constituents. In this connection the crude oil would be passed or injected into a chamber maintained at subatmospheric pressure in which the lighter fractions of the crude oil would be immediately vaporized. The latent heat required for vaporization of light fractions cools the liquid portion of the crude oil to a sufficiently low temperature at which the wax crystals will precipitate and entrain the particles of salt water.

The so treated unvaporized portion of the crude oil will then be passed into a zone in which the wax crystals and salt water may be settled out or the cooled liquid portions of the crude may be subjected to filtration for removal of the wax crystals and the entrained salt water. This method of refrigeration is particularly applicable to crude oils having a fairly high vapor pressure such as is the case of East Texas crude oils.

The reduced pressure in the low pressure or flash chamber may be maintained by any suitable means such as vacuum pumps or ejectors. Also, the vapors removed from the crude oil in the zone of reduced pressure may be recovered by absorption, adsorption, or compression followed by condensation or any other method suitable for such recovery of the vapors. A reduced pressure may be maintained in the reduced pressure zone by the use of gas oil in a jet or barometric leg and the gas oil would also serve as an absorbing medium for the vapors evolved from the crude.

In some cases where the viscosity of the crude oil is very high under the reduced filtering or settling temperatures, a light naphtha cut may be added for the purpose of reducing the viscosity to a point where filtration will be facilitated. The light naphtha added will also aid in any settling operation inasmuch as it will increase the difference in gravity between the cooled crude oil and the salt-wax mixture.

In lieu of internal refrigeration by evaporation of the light constituents of the crude oil in a vacuum chamber, internal refrigeration of the crude oil may be obtained by cycling or recycling a normally gaseous hydrocarbon such as propane along with the crude oil. In this instance, liquid propane is added to the incoming crude oil and then allowed to evaporate. The heat of vaporization of the propane will cool the crude oil sufficiently to precipitate the existing or added wax therein and as in the preceding instances will entrain the salt water contained in the crude oil. The propane may be recovered by compression and condensation and re-cycled in the process.

Referring to the accompanying drawing, there is shown a system for desalting crude oil utilizing both internal refrigeration and re-cycling of wax. As shown in the drawing, the salty crude oil is pumped to a storage container 1 from which it is drawn by the pump 2 and forced through conduit 3 into the low pressure zone 4. A reduced pressure is maintained in the zone 4 by means of the pump 5 which draws gas and vapors from the upper portion of zone 4 through the conduit 6.

The salt containing crude oil is pumped from the storage tank into the low pressure zone and may be ejected into said zone in such a manner as to effect a flashing or vaporization of the lighter constituents thereof. As explained above, the flashing of the crude oil will effect internal refrigeration of the non-vaporized portions which will collect in the lower regions of the zone 4. The cool liquid portions of the crude oil together with the precipitated wax and entrained salt water are then drawn from the zone 4 by means of a suitable pump 7 into a filter 8 in which the crystallized wax particles together with the entrained salt water are separated from the oil. The desalted crude is then discharged through the conduit 9 to a storage vessel (not shown).

Filter 8 may be of any suitable type effective for the purpose and the wax and entrained salt water separated in the filter are discharged into a heating zone 10 containing a heating coil 11. In the heating zone 10, the mixture of wax and salt water is heated to melt the wax and the mixture of liquid wax and salt water is passed through conduit 12 into the wax settler 13. From the lower portion of the settler 13 the salt water is drawn off and from an upper portion thereof the wax portion is discharged through conduit 14. Of the wax removed from the wax settler 13, a portion is re-cycled for introduction into the conduit 3 for conducting the crude oil to be treated into the low pressure zone 4. This wax in liquid form is introduced through conduit 15. Wax discharged through conduit 14 in excess of that required for re-cycling is discharged from the system through conduit 16.

In the event of insufficient wax in the crude further wax may be added through conduit 28.

If desired, the cooled desalted crude discharged through conduit 9 may be passed in heat exchange relation with the crude oil prior to introduction of the crude into the reduced temperature zone. For this purpose the cold desalted oil is passed through conduit 17 to the cooling heat exchanger 18 and thence through conduit 17a to storage.

If the temperature of the crude oil to be desalted and requiring the addition of further wax for desalting is too low to receive additional wax, the cold oil may be passed through a heat exchanger 19 which is heated by a suitable medium. This will heat the cold crude oil to a temperature high enough to dissolve the desired quantity of added wax.

If the crude has already been stripped of its lighter fractions prior to the desalting treatment, or if insufficient internal refrigeration is obtained by flashing the crude, a normally gaseous hydrocarbon such as propane in the liquid phase may be introduced into the crude oil. As indicated in the drawing, liquid propane is introduced into the crude supply line 3 of the system through conduit 20 between heat exchangers 18 and 19. When the crude containing the propane passes into the low pressure zone 4 the vaporization of the propane will cool the oil to cause precipitation of the wax. Vaporized propane is withdrawn from the flash chamber or low pressure zone 4 by compressor 5, compressed and passed through conduit 21 which includes a condenser 22. The condensed liquid propane is then re-cycled through conduit 20 into the system.

It is also within the concept of the present invention to effect the desalting of crude oil by entraining the salt water in precipitated wax crystals, permitting settling of the precipitated wax crystals in a quiescent zone, and then melting the settled wax layer without setting up substantial convection currents therein. For this purpose a crude oil containing the precipitated wax and entrained salt water may be run through a conduit 23 into a quiescent zone 24 in which the wax is allowed to settle. After settling of the wax, the oil is heated from a coil 25 or other source positioned above the wax layer so that the wax layer will be melted sufficiently to free the entrained salt water without creating sufficient convection currents to agitate the melted wax and salt water sufficiently to again mix the same. Under these conditions, the freed salt water would settle out at the bottom of the zone and may be drawn off from the layer of melted wax as indicated at 26, the salt free oil together with the wax being drawn off at 27.

While I have shown methods of separation involving generally the use of a settling operation or a filter, other known methods of separating the crude oil from the salt-wax mixture may be used. For example, centrifugal separating means may be used. In this case, the mixture from the flash chamber 4 would be pumped to a regular centrifuge where the wax and salt water would be removed from the crude oil. In such an operation, by introducing hot water into the wax-salt water stream, the salt water may be diluted and the wax melted so that the mixture leaving the centrifuge can be separated into its two constituents by the use of ordinary settling tanks. When internal methods of refrigeration are not used, the effluent from cooler 18 can be passed directly to the centrifuge and treated as described above. Separation by such centrifugal methods would usually be advantageously used where the type of wax crystal is of an amorphous character. In such an operation, the presence of the salt water actually facilitates the wax separation since it tends to increase the difference in gravity between the crude oil and the wax due to the occlusion of the relatively heavy salt water in the wax.

In those instances in which wax is added to a crude oil having a low wax content, the added wax should be of such a nature as to be easily separated from the oil upon precipitation. Likewise, the wax selected should have properties which will facilitate the entrainment of the salt water contained in the oil.

From the foregoing description it will be appreciated that the present invention provides several procedures for effectively desalting crude oil by removing existing or added wax and salt water entrained therein or by merely effecting settling of the precipitated wax and entrained salt water and then effecting a gravity separation of the wax and entrained salt water without physical removal of the wax from the crude oil.

I claim:

1. A method of treating crude mineral oil which comprises maintaining an intimate mixture of fluid wax and salt-containing mineral oil at above atmospheric temperature, cooling said mixture to precipitate solid wax and entrained salt, separating the wax and entrained salt from the oil, recovering desalted oil, and effecting separation between the wax and the entrained salt.

2. A method of desalting crude mineral oil which comprises maintaining an intimate mixture of fluid wax and salt-containing mineral oil at above atmospheric temperature, cooling said mixture to precipitate solid wax having salt entrained therein, separating the wax and entrained salt from the oil, recovering desalted oil, effecting separation of the wax and the entrained salt, and commingling substantially salt-free wax with additional amounts of salt-containing crude mineral oil.

3. A method of desalting crude mineral oil comprising adding wax thereto, cooling the oil to effect precipitation of the wax contained therein in admixture with salt and separating the precipitated material.

4. A method of removing salt from crude mineral oil comprising heating the same to a temperature below that at which low boiling fractions will separate, adding crystallizable wax to the heated oil, cooling the wax containing oil

to precipitate wax crystals admixed with salt and separating the precipitated crystals.

5. A method of desalting crude mineral oil comprising introducing a liquefied normally gaseous hydrocarbon into the wax and salt containing mineral oil, effecting evaporation of the added hydrocarbon to chill the mineral oil and precipitating a mixture of the wax and salt and separating the precipitated wax-salt emulsion.

6. A method of desalting crude mineral oil comprising heating the oil to a temperature above atmospheric, dissolving a quantity of wax therein, cooling the oil to atmospheric temperature to effect a precipitation of the added wax in the form of a salt water entraining crystals and then separating the precipitated material.

7. A method of desalting crude mineral oil having a high vapor pressure and containing precipitatable wax comprising passing the oil into a zone at a reduced pressure to effect vaporization of the light portions of the oil and consequent refrigeration thereof, thereby precipitating the wax in the form of salt water entrained crystals and separating the precipitated material.

8. A method of desalting crude mineral oil comprising passing the oil under pressure into a zone of reduced pressure to cause the light fractions thereof to vaporize with consequent cooling of the remaining liquid portions of the oil and precipitation of wax crystals mixed with salt, separating the precipitated crystals, heating the separated mass to separate the wax from the salt water, and mixing the separated wax with fresh portions of crude mineral oil to be desalted prior to cooling of the same.

9. A method of removing salt from crude mineral oil comprising heating the oil to a temperature below that at which low boiling fractions will separate, adding wax to the heated oil, cooling the wax containing oil and expanding the same into a zone of reduced pressure to effect further cooling of the unvaporized portions of the oil and to effect precipitation of wax in the form of crystals entraining salt, and separating the precipitated crystals.

10. A method of removing salt from crude mineral oil comprising heating the oil to a temperature below that at which low boiling fractions will separate, adding wax to the heated oil, cooling the wax containing oil and expanding the same into a zone of reduced pressure to effect further cooling of the unvaporized portions of the oil and to effect precipitation of wax in the form of crystals entraining salt, and circulating the cool wax-free and salt-free oil in heat exchange relation with the oil to be treated after addition of wax thereto to effect pre-cooling of the oil to which the wax has been added.

11. A method of removing salt from crude mineral oil comprising heating the oil to a temperature below that at which low boiling fractions will separate, adding wax to the heated oil, cooling the wax containing oil and expanding the same into a zone of reduced pressure to effect further cooling of the unvaporized portions of the oil and to effect precipitation of wax in the form of crystals entraining salt, treating the separated wax and salt water material to separate the wax from the salt water, and re-introducing the wax into crude oil to be treated prior to cooling thereof.

12. A method of desalting crude mineral oil comprising cooling the oil to effect precipitation of wax crystals containing entrained salt water, effecting settling of the precipitated material and heating the settled layer of the precipitate in a manner to avoid substantial convection currents to melt the wax of said settled layer and then separating the salt water from the melted layer of wax.

13. The method of desalting crude mineral oil which comprises intimately mixing liquid wax and salt-containing mineral oil, cooling the intimate mixture sufficient to precipitate solid wax with entrained salt, separating solid wax and entrained salt from said mineral oil, and recovering the desalted oil.

CHALMER G. KIRKBRIDE.