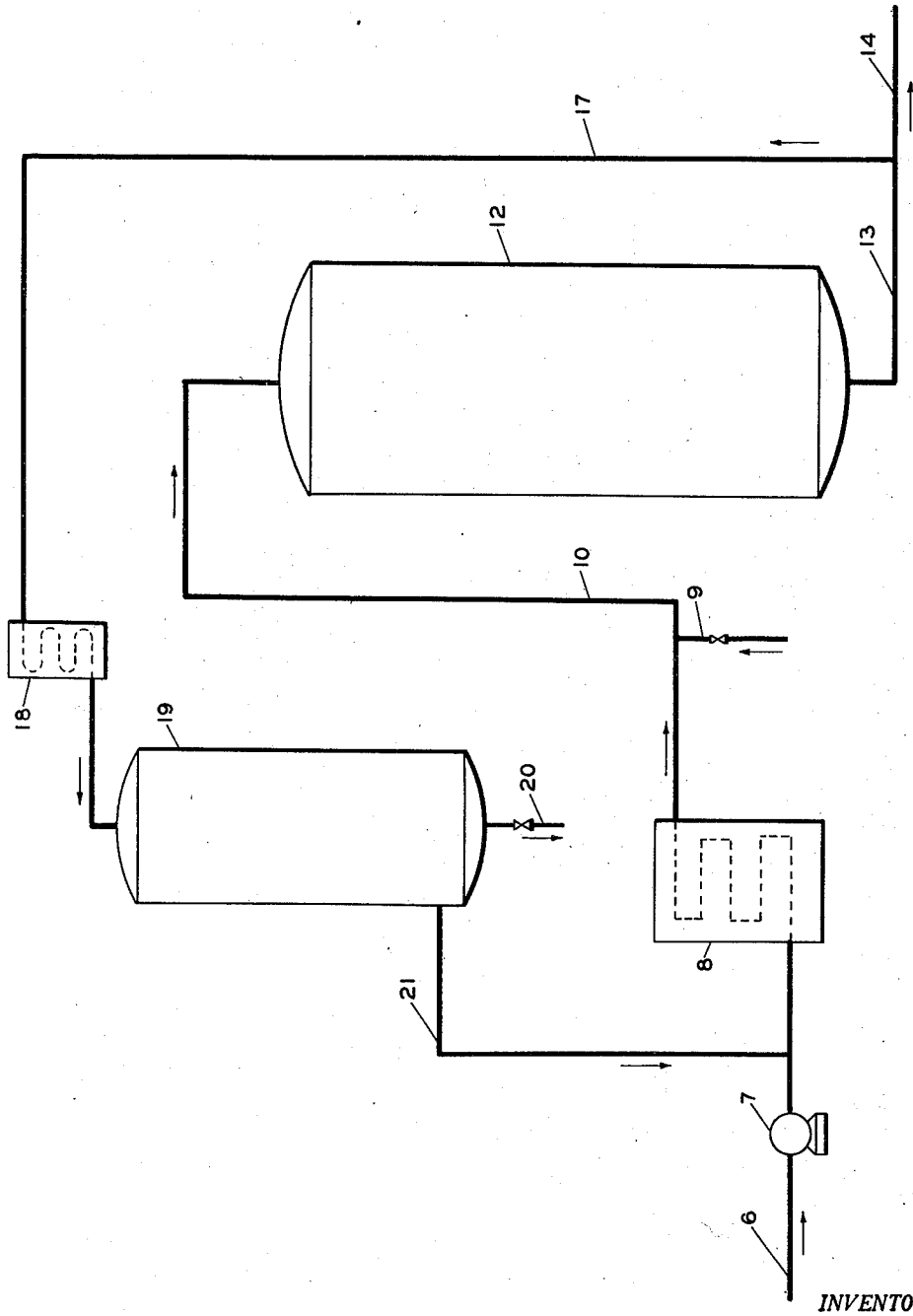
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TREATMENT OF HYDROCARBON OILS

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TREATMENT OF HYDROCARBON OILS

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This invention relates to the treatment of sour hydrocarbon oils to sweeten the same. In one of its more specific aspects, this invention relates to the removal of water of reaction from a system utilized in the sweetening of natural gasoline, refinery straight run and cracked gasolines, petroleum solvent naphthas, liquefied petroleum gases, kerosenes, and the like, to convert the sulphur compounds such as mercaptans therein which are responsible for bad odors or sourness and for corrosiveness of these hydrocarbon materials. In another of its more specific aspects, this invention relates to improvement in the sweetening of mercaptan-bearing light hydrocarbon materials by means of a moist solid reagent comprising a copper salt and a halide adsorbed on carriers.

Such unrefined petroleum products contain mercaptans, commonly called "sour" elements, which give the product an undesirable odor. These compounds have sometimes been altered, by the so-called "doctor" process, a laborious, cumbersome and very uneconomical chemical treatment with alkali plumbite and sulfur. In some instances, e. g. with a natural gasoline, the sweetening reaction has been accomplished through the use of alkaline hypochlorite solutions, but this method, too, has not proved satisfactory in most cases. Sometimes the "sour" elements seem to be particularly difficult to sweeten, thereby requiring large quantities of the reagent, and in other cases the treatment seems to result in the introduction into the oil of undesirable constituents as bad as those originally present. Still other methods have been suggested for removal or conversion of the mercaptans but almost without exception these methods involve numerous treating steps which demand such close control of the operation that the operating costs are increased so much as to render such methods uneconomical.

Successful, economical methods of sweetening which have now come into common use are so-called copper sweetening processes which are now well known in the petroleum industry. One such process is described by Buell in U. S. Patent 2,094,485. In that type of process a solid treating agent comprising a highly porous or adsorbent material such as fuller's earth, charcoal, or the like, is impregnated with a concentrated solution

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of cupric chloride, or other cupric halide, or of a water-soluble cupric salt, such as cupric sulfate, and a halide, such as sodium chloride. A stream comprising a mercaptan, such as a "sour" hydrocarbon material, is contacted with said reagent by passing it in the liquid state, together with dissolved oxygen-containing gas, at ordinary temperatures through the reagent bed.

When mercaptans are passed in such a process over such a copper halide-containing reagent the following type of reaction occurs:

(1) $4CuCl_2 + 4R{-}SH \longrightarrow 2R{-}S{-}SR + 4CuCl + 4HCl$

Cupric chloride — Mecaptan — Alkyl disulfide — Cuprous chloride — Hydrochloric acid

Thus it is seen that the mercaptans are converted to less objectionable disulfides while the cupric compound is reduced to the cuprous state and hydrochloric acid is formed.

In order to maintain the activity of the solid copper containing reagent it is necessary to add to the hydrocarbon material prior to its passage over the reagent a sufficient quantity of oxygen, air, or an equivalent gas to supply oxygen to regenerate the spent reagent according to this reaction:

(2) $4CuCl + 4HCl + O_2 \rightarrow 4CuCl_2 + 2H_2O$

Thus when free oxygen is in solution with the hydrocarbon material at the time of sweetening, reactions 1 and 2 occur simultaneously and the reagent is maintained in an active state.

From reaction (2) however, it is apparent that another undesirable situation arises in that considerable amounts of water are formed in maintenance of the reagent in an active state. This water, unless carried out by the product stream, tends to saturate the reagent and frequently causes shutdowns so that the reagent can be dehydrated. In attempting to overcome this trouble, it has been common practice to install in the feed stream, a salt filter, sand filter or other means to remove any free or entrained water from the feed and following this to preheat the feed stream at some point ahead of the copper treating tower. The preheating increases the capacity of the feed stream to dissolve water therein. Having a greater capacity to dissolve water, the feed stream will tend to dissolve more of the water of reaction and to carry more of

it out of the reagent tower than it would at lower temperatures. This practice however frequently fails to remove an amount of water sufficient to prevent the reagent from rapidly becoming saturated.

An object of the invention is to provide an improvement for copper sweetening processes whereby the sweetening of a very sour light hydrocarbon material by means of a solid reagent comprising a solution of copper salt and a halide adsorbed on a solid adsorbent carrier material may be accomplished efficiently and economically for more extended periods of time.

A further object of the invention is to substantially reduce the number of shutdowns required in a copper sweetening unit to dehydrate the reagent.

A still further object of the invention is to provide an improved process for converting mercaptans to disulfides.

Still other objects and advantages will be apparent to those skilled in the art from a careful study of the accompanying detailed disclosure.

I have now discovered an important improvement in converting mercaptans to disulfides, such as in the sweetening of a light or low boiling hydrocarbon material according to the previously described process utilizing a solid copper-containing reagent when the mercaptan content of the "sour" hydrocarbon is so great that the resultant water produced tends to saturate the reagent in a relatively short period of time. This process of converting mercaptans to disulfides is generally used in the sweetening of a "sour" hydrocarbon stream wherein the mercaptan concentration is relatively small. It may, however, be used in a process for commercially converting mercaptans to disulfides wherein the mercaptan concentration in relation to its hydrocarbon or other diluent which is non-reactive with the reagent, is relatively large. The improvement comprises recycling a portion of the product stream, cooling the recycled stream to precipitate water formed during the process of converting the mercaptans, passing it through a filter to separate out free water, and adding the thus partially-dried recycled stream to the feed stream. In this manner substantial amounts of water are removed from the recycled stream thus making the parts of water per unit of material treated substantially the same as that contained in the original feed stream, but with a greater hydrocarbon volume and therefore a capacity to remove or carry larger quantities of water in solution. Water may be removed from this recycle stream if desired, by cooling to a low temperature, and/or by contact with a suitable desiccant, such as bauxite, silica gel, calcium chloride, or the like. This combined stream is then heated, to substantially increase the moisture absorbing potential of the stream, and is then passed through the copper reagent chamber. It will also be noted that by recycling a portion of the sweetened product a decrease in mercaptan content per unit of combined feed is obtained, although the same amount of mercaptan would be passed through the reactor and the same amount of water would be formed as if no recycle were used. At the same time, however, the recycle "sweet" hydrocarbon will dissolve as much water proportionally as the "sour" net charge with the advantage that it will not cause the formation of free water. By operation in this manner it is possible for the copper reagent tank to be maintained on stream for substantially much greater periods of time without shutdowns for the purpose of dehydrating the reagent.

Referring now to the accompanying diagrammatic drawing, the original temperature of the light or low boiling hydrocarbon oil which is introduced into the system through line 6 and pump 7 is generally substantially that of the atmosphere. As it passes through heater 8 it is raised to a temperature between about 110° F. and about 130° F., preferably about 120° F. In this manner the moisture absorbing potential of the oil is substantially increased. Air or an equivalent gas which is needed to furnish the essential oxygen for reactivation of the reagent is supplied to the system through line 9. Oxygen may be injected instead of air but air is generally used for purposes of economy. There is nothing critical about the point at which the air is to be injected. Equally as efficient results are obtained by introducing air to the feed stream before heating as after the heating step. Usually the air is injected at a pressure of between about 25 and about 50 pounds per square inch, but such pressure is limited only by the operating pressure limit of the plant equipment, usually from about 15 to about 100 pounds per square inch. The amount should be sufficient to effect complete regeneration, based on complete conversion of mercaptans to disulfides, in accordance with the previously discussed reactions. The heated feed is introduced through line 10 into reagent chamber 12 where the reaction, above described, takes place. Sweetened hydrocarbons are removed through line 13 and are directed to storage through line 14. A portion of the sweetened oil is drawn off through line 17 and is supplied to dehydration means, such as cooler 18 and water-filter 19. In cooler 18 the temperature of the sweetened hydrocarbon stream is reduced to a point between about 60° F. and about 90° F., but preferably to about 80° F. In this manner the ability of the hydrocarbon stream to carry dissolved water is reduced and substantial amounts of water which were formed in the sweetening reaction and carried in the hydrocarbon stream are precipitated. It is obvious that some additional water may be separated from the oil stream by cooling below 60° F., and a desiccant may be used in conjunction with or in place of such a cooler and filter, but in most instances it is unnecessary and uneconomical to do so. The hydrocarbon stream is then passed from cooler 18 to filter 19 where the entrained water is removed. Any conventional material may be used in the filter to coalesce and remove the condensed water out of the hydrocarbon stream. I prefer to use either sand or salt. Water which has been removed from the recycle stream is drained off through line 20 while the stream is fed through line 21 to the feed stream in line 6. As the amount of mercaptan will remain constant and the volume of water of formation is the same, saturation of the reaction chamber will be substantially reduced by means of the recycle portion because the portion of the stream which is already sweetened will take up its portion of the water but will not cause water to be formed.

In the following table a "material balance" is shown for a copper sweetening operation with and without recycle when charging a "sour" gasoline weighing 260 pounds per barrel with a mercaptan (RSH) content of 0.03 weight per cent and entering the unit at 80° F. and being heated to 120° F. The recycle operation utilizes a recycle ratio of 1:1.

Table I

Operation Stream	With Recycle							Without Recycle		
	Line 6	Line 10	Line 13	Line 14	Line 17	Line 21	Line 20	Line 6	Line 10	Lines 13 and 14
Barrels/Day	240	480	480	240	240	240		240	240	240
Barrels/Hour	10	20	20	10	10	10		10	10	10
Temperature	80	120	120	120	120	80		80	120	120
Per cent RSH (Mercaptan)	0.03	0.015						0.03	0.03	
H_2O: Parts per Million	105	105	240	240	240	105		105	105	240
Per cent Saturation	100	44	100	100	100	100		100	44	100
Pounds/Barrel	.0273	.0273	.0624	.0624	.0624	.0273		.0273	.0273	.0624
Pounds/Hour	.273	.546	1.248	.624	.624	.273	.351	.273	.273	.624
Pounds/Day	6.552	13.104	29.952	14.976	14.976	6.552	8.424	6.552	6.552	14.976

The following table discloses data which show clearly the effect the invention has on the operating time for a copper sweetening unit. These data based on the preceding material balance are for a unit utilizing 2,000 pounds of reagent.

Table II

Operation	With Recycle		Without Recycle	
Water, Pounds/Day:				
In Charge Stream	6.552		6.552	
Formed in Sweetening Reaction	21.048		21.048	
Total	27.600	27.600	27.600	27.600
Water Eliminated:				
In Sweetened Product	14.976		14.976	
By Recycle	8.424			
Total	23.400	23.400	14.976	14.976
Water Remaining in Reagent, Pounds/Day		4.200		12.624
Permissible Accumulation in Reagent	260		260	
Days Operation Before Dehydrating	62		20	

It is apparent that a great deal of flexibility is possible in this method of controlling the water content of the reagent by varying the amounts of the sweetened hydrocarbon which are recycled to the sour feed stream, the amount of water removed from the recycle stream, and methods for partially dehydrating said recycle stream. The maximum allowable water content of the reagent bed is generally substantially 28 to 30 weight per cent.

I claim:

1. In a process for sweetening a sour low boiling hydrocarbon stream which comprises the steps of heating said stream, furnishing oxygen to said stream, contacting said stream with a reagent comprising an adsorbent material impregnated with a copper salt and a halide in the presence of a small portion of water, and withdrawing a sweetened hydrocarbon from contact with said reagent; the improvement which comprises the steps of cooling a portion of said sweetened hydrocarbon so as to precipitate in said hydrocarbon water formed in the sweetening of said hydrocarbon, separating said precipitated water therefrom, combining said sweetened and dehydrated stream with said sour feed stream, contacting said combined feed stream with said reagent, and removing a portion of water formed during said sweetening step from said reagent by dissolving said water in said sweetened and dehydrated portion of said feed stream.

2. In a process for sweetening a sour low boiling hydrocarbon stream which comprises the steps of heating said stream to a temperature between about 110° F. and about 130° F., furnishing oxygen to said stream, contacting said stream with a reagent comprising an adsorbent material impregnated with a copper salt and a halide in the presence of a small portion of water, and withdrawing a sweetened hydrocarbon from contact with said reagent; the improvement which comprises the steps of cooling a portion of said sweetened hydrocarbon to a temperature between about 60° F. and about 90° F. so as to precipitate in said hydrocarbon water formed in the sweetening of said hydrocarbon, separating said precipitated water therefrom, combining said sweetened and dehydrated stream with said sour feed stream, contacting said combined feed stream with said reagent, and removing a portion of water formed during said sweetening step from said reagent by dissolving said water in said sweetened and dehydrated portion of said feed stream.

3. In a process for sweetening a sour low boiling hydrocarbon stream which comprises the steps of heating said stream to a temperature between about 110° F. and about 130° F., dissolving air in said stream, contacting said stream with a reagent comprising an adsorbent material impregnated with a copper salt and a halide in the presence of a small portion of water, and withdrawing a sweetened hydrocarbon from contact with said reagent; the improvement which comprises the steps of cooling a portion of said sweetened hydrocarbon to a temperature between about 60° F. and about 90° F. so as to precipitate in said hydrocarbon water formed in the sweetening of said hydrocarbon, passing said sweetened hydrocarbon through a filter to remove said precipitated water from said stream, combining said sweetened and dehydrated stream with said sour feed stream, contacting said combined feed stream with said reagent, and removing a portion of water formed during said sweetening step from said reagent by dissolving said water in said sweetened and dehydrated portion of said feed stream.

4. In a process for converting mercaptans to disulfides which comprises the steps of heating a hydrocarbon mercaptan-containing stream, furnishing oxygen to said stream, contacting said stream with a reagent comprising an adsorbent material impregnated with a cupric halide in the presence of a small portion of water, withdrawing a disulfide-containing stream from contact with said reagent; the improvement which comprises the steps of partially dehydrating a portion of said disulfide-containing stream, combining said partially dehydrated disulfide-containing stream with said mercaptan-containing stream, contacting said combined streams with said reagent, and removing a portion of water which is formed in the conversion of the mercaptant to disulfide by dissolving said water in said partially dehydrated disulfide-containing stream.

5. The process of claim 4, wherein oxygen is furnished by means of the introduction of air to said stream.

6. In a process for converting mercaptans to disulfides which comprises the steps of heating a hydrocarbon mercaptan-containing stream, furnishing oxygen to said stream, contacting said stream with a reagent comprising an adsorbent material impregnated with a copper salt and a halide in the presence of a small portion of water, and withdrawing a hydrocarbon disulfide-containing stream from contact with said reagent; the improvement which comprises the steps of partially dehydrating a portion of said disulfide stream, combining said partially dehydrated disulfide-containing stream with said mercaptan-containing stream, contacting said combined stream with said reagent, and removing a portion of water formed in the conversion of the mercaptans to disulfides by dissolving said water in said partially dehydrated disulfide-containing stream portion.

7. The process of claim 4, wherein oxygen is furnished by means of the introduction of air to said stream.

8. In a process for sweetening a sour low boiling hydrocarbon stream which comprises the steps of heating said stream, furnishing oxygen to said stream, contacting said stream with a reagent comprising an adsorbent material impregnated with a cupric halide in the presence of a small portion of water, and withdrawing a sweetened hydrocarbon from contact with said reagent; the improvement which comprises the steps of cooling a portion of said sweetened hydrocarbon so as to precipitate in said hydrocarbon water formed in the sweetening of said hydrocarbon, separating said precipitated water therefrom, combining said sweetened and dehydrated stream with said sour feed stream, contacting said combined feed stream with said reagent, and removing a portion of water formed during said sweetening step from said reagent by dissolving said water in said sweetened and dehydrated portion of said feed stream.

9. In a process for sweetening a sour low boiling hydrocarbon stream which comprises the steps of heating said stream to a temperature between about 110° F. and about 130° F., dissolving air in said stream, contacting said stream with a reagent comprising an adsorbent material impregnated with a cupric halide in the presence of

a small portion of water, and withdrawing a sweetened hydrocarbon from contact with said reagent; the improvement which comprises the steps of cooling a portion of said sweetened hydrocarbon to a temperature between about 60° F. and about 90° F. so as to precipitate in said hydrocarbon water formed in the sweetening of said hydrocarbon, passing said sweetened hydrocarbon through a filter to remove said precipitated water from said stream, combining said sweetened and dehydrated stream with said sour feed stream, contacting said combined feed stream with said reagent, and removing a portion of water formed during said sweetening step from said reagent by dissolving said water in said sweetened and dehydrated portion of said feed stream.

10. The process of claim 9 wherein said filter is a sand filter.

11. The process of claim 9 wherein said filter is a salt filter.

12. In a process for sweetening a sour low boiling hydrocarbon stream which comprises the steps of heating said stream, furnishing oxygen to said stream, contacting said stream with a reagent comprising an adsorbent material impregnated with a copper salt and a halide in the presence of a small portion of water, and withdrawing a sweetened hydrocarbon from contact with said reagent; the improvement which comprises the steps of partially dehydrating said sweetened stream, combining said sweetened and partially dehydrated stream with said sour feed stream, contacting said combined feed stream with said reagent, and removing a portion of water formed during said sweetening step from said reagent by dissolving said water in said sweetened and partially dehydrated portion of said feed stream.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
Re. 20,938	Hoover	Dec. 6, 1938
2,264,220	Schulze	Nov. 25, 1941
2,297,650	Fry et al.	Sept. 29, 1942
2,315,820	Schulze et al.	Apr. 6, 1943