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METHOD OF DISSOLVING ASPHALTENE DEPOSITS

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This invention relates to solvents for asphaltene and heterogeneous solid deposits which include asphaltene.

The term "asphaltene" is applied to those components of petroleum which are dark-colored, amorphous, neutral with respect to acids and alkalies, insoluble in light paraffinic hydrocarbons (specifically, petroleum ether), and soluble in benzene, chloroform, or carbon disulfide. They are polycyclic aromatic compounds of very high molecular weight containing not only carbon and hydrogen but also oxygen or sulfur or both and, in some cases, a substantial proportion of nitrogen. At ordinary temperatures such solutions as they form are colloidal. At higher temperatures, for example 120° C., the molecular weights are much decreased and the asphaltene are capable of forming true solutions.

When asphaltene occur in petroleum, they may be colloiddally dissolved or may be in the form of suspended solid particles. Under some conditions the suspended particles adhere to oil-well tubing, pipe lines, etc., and the colloidal asphaltene are subject to deposition by electrical effects created by motion of the petroleum and by ground currents. In gas wells, deposits of bituminous material including large proportions of asphaltene are sometimes formed by evaporation of the hydrocarbon liquids collecting in the bottoms of the wells. The deposits formed in these ways often include other solids such as sand, clay, and wax, with the asphaltene acting as the principal cementing material. Such deposits are hard, extremely tenacious, and most difficult to remove by scraping, washing, or any other method which has been employed heretofore.

Numerous solvents for asphaltene are known in the art. However, those which are efficient, such as carbon disulfide, nitrobenzene, and pyridine, are costly, dangerous to handle, or both. The relatively safe and inexpensive solvents such as benzene and Edeleanu extracts of cracked petroleum distillates are so slow in their action and have so little capacity for asphaltene that their use requires excessive amounts of time and material.

I have discovered that mixtures of hydrocarbon liquids with acetone or a similar ketone are good solvents for asphaltene and are fully suitable for cleaning hard black deposits from oil wells, gas wells, and pipelines. This is unexpected, because the ketones themselves are very poor solvents for asphaltene and were not known to have any property which would result in creation of solvent power for asphaltene in their mixtures.

In the case of colorless hydrocarbon liquids of paraffinic, olefinic, or naphthenic nature, which dissolve asphaltene to a negligible degree or not at all, I have tested ketone mixtures by placing a small lump of asphaltene material in a test tube, adding some of the mixture to be tested, shaking the tube, and observing the degree and rapidity of darkening of the liquid by dissolved asphaltene.

In this manner I have examined numerous mixtures of acetone, 2,4-pentanedione, and diacetone alcohol with gasoline, kerosene, A.S.T.M. naphtha, rubber solvent,

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and various narrow petroleum fractions of different degrees of volatility and saturation which are prepared for use as solvents and designated by trade names. In each case, I have found that ketone-hydrocarbon mixtures within the range of about five to forty percent by volume of the ketone are good solvents for asphaltene, sufficiently effective to be used for the removal of asphaltene deposits from pipe lines and the like.

In the case of aromatic hydrocarbon liquids, which have fairly good solvent power for asphaltene without addition of a ketone, the simple visual technique is not satisfactory. I have tested mixtures of such liquids with ketones by the following procedure. A suspension of asphaltene in the hydrocarbon liquid is prepared by dissolving a measured amount of dehydrated asphaltene in a measured amount of the liquid at an elevated temperature. Equal amounts of the suspension are poured into each of two centrifuge tubes. To one of the tubes is added enough ketone to form the solvent mixture to be tested, and the same amount of the hydrocarbon is added to the other tube. The two tubes are whirled in a centrifuge for about fifteen minutes, and then the amount of precipitated asphaltene in each tube is observed.

In all cases, I have found that addition of acetone and similar ketones to aromatic hydrocarbon liquids causes a remarkable increase in solvent power for asphaltene.

I have not investigated the normally gaseous hydrocarbons, such as butane, nor the viscous hydrocarbon liquids, such as lubricating oil, because such substances are obviously not practical as components of solvent mixtures for use in the oil fields. But within the class of normally liquid hydrocarbons of low viscosity, it is apparent that addition of an aliphatic ketone, up to at least C₆, always increases solvent power for asphaltene, whether the hydrocarbon be paraffinic, olefinic, naphthenic, or aromatic, and whether the unassisted hydrocarbon be capable of dissolving asphaltene or not.

For use upon deposits which consist predominantly of asphaltene or of mixtures of asphaltene with insoluble matter such as sand and clay, I prefer to employ a mixture of acetone and an aromatic hydrocarbon liquid such as Edeleanu extract from petroleum distillates, and it is in some cases desirable to add a hydroxy-aromatic material such as cresylic acid, which acts as a softening agent and thus facilitates the attack of the solvent mixture upon extremely hard deposits.

The Edeleanu extract I have employed has the following properties:

50 Gravity	-----	° A.P.I.	26.0
A.S.T.M. distillation:			
Initial	-----	° F.	340
10%	-----	° F.	373
50%	-----	° F.	425
90%	-----	° F.	487
End point	-----	° F.	520
Olefines and aromatics	-----	percent	75-82
Bromine number	-----		4-8

The maximum solvent power of mixtures of this liquid with acetone occurs at 65% by volume of the Edeleanu extract and about 35% acetone. This mixture was tested as follows:

Five grams of dehydrated asphaltene was dissolved in 130 cc. of Edeleanu extract by heating to about 300° F. The resulting suspension was divided equally and placed in two graduated centrifuge tubes. Enough acetone was added to one tube to bring the level up to 100 cc., and enough Edeleanu extract was added to the other to bring the contents to the same level. The tubes were then thoroughly shaken and placed in a centrifuge for fifteen minutes. When the tubes were examined, it was found that about 2 cc. of dark precipitate had settled out in the

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tube which contained no acetone, and in the tube which contained about 35% acetone only a few tenths of one cubic centimeter had settled out.

There is little evidence that anything in the nature of chemical combination of ketones and hydrocarbons occurs; however, it is interesting to note that the proportion of acetone and Edeleanu extract which has the greatest solvent power coincides with the proportion which yields the greatest temperature drop upon formation of the mixture. When various mixtures were prepared, the temperature drop was observed and the following results noted:

Proportion Edeleanu Extract, Percent	Proportion Acetone, Percent	Temperature Drop, °F.
80	20	6
70	30	8
65	35	9
60	40	7.5
55	45	7

For use upon deposits which contain substantial proportions of wax in addition to the asphaltenes and inorganic material, it is preferable to use a predominantly paraffinic hydrocarbon liquid of moderately low average molecular weight, such as gasoline.

It is often desirable to employ mixtures which include much less of the ketone than that required to yield the maximum solvent power for asphaltenes. In some cases the reason is merely economic, depending on the fact that a mixture containing relatively little ketone may yield adequate results at lower cost. But in other cases the usefulness of the composition is involved, as when it is preferred that the solvent power of the hydrocarbon for wax not be diminished by the addition of too much ketone.

A number of solvent compositions consisting of or including mixtures of hydrocarbons with acetone have been successfully employed in the field. The following two have been found to be fully satisfactory and are now in regular use in California oil and gas fields.

Composition A:	Percent by volume
Edeleanu extract	55
Acetone	10
Cresylic acid	35
Composition B:	
Unleaded aviation gasoline	67
Acetone	33

The Edeleanu extract is derived from a kerosene distillate and is essentially the same material as that described above, with some slight variations in the gravity and distillation range. The aviation gasoline has the following specifications:

Gravity	66° A.P.I.
A.S.T.M. distillation:	
10%	Max. 167° F.
40%	Min. 167° F.
50%	Min. 221° F.
90%	Max. 275° F.
End point	338° F.

Composition "A" is chosen for dissolving the hard, coke-like deposits which contain little organic material

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except asphaltenes. For example, in the case of an 11,000-foot gas well which was almost completely clogged with such a deposit, the well was shut down in the late afternoon and about a barrel of composition "A" was injected. The well remained shut down overnight, and it was reopened at about nine o'clock the next morning and permitted to blow itself out with its own pressure. The well was then able to produce gas at its full capacity, and subsequent testing with a feeler showed no indication of any remaining deposit. The previous time the same well had become clogged there had been a completely unsuccessful attempt to dissolve the deposit with Edeleanu extract, and it was necessary to remove the deposit by drilling. Composition "A" has been used numerous times in similar wells, with dosages of from half a barrel to a barrel.

Composition "B" is chosen for dissolving deposits, common in lead lines and other piping, which include considerable amounts of wax together with asphaltenes and inorganic matter. These deposits are softer and usually more accessible, and yet they have presented a serious problem because heretofore the wax and the asphaltenes have not been subject to the same solvents or mixtures of solvents, and each has tended to protect the other from the solvents which might have been effective.

The present application is a continuation-in-part of my copending application Serial No. 356,608, filed May 21, 1953, now abandoned.

I claim as my invention:

1. A process of removing from oil and gas wells and from petroleum pipe lines deposits which include asphaltenes and which are substantially devoid of readily petroleum-soluble materials, comprising: exposing said deposits to the solvent action of a mixture including a liquid-sulfur-dioxide extract from a petroleum distillate and acetone, said mixture containing about five to forty percent by volume of acetone.

2. A process of removing from oil and gas wells and from petroleum pipe lines those hard, black deposits which include asphaltenes and which are substantially devoid of readily petroleum-soluble materials, comprising: exposing said deposits to the solvent action of a mixture of about 55% by volume of a liquid-sulfur-dioxide extract from a petroleum distillate, about 10% by volume of acetone, and about 35% by volume of cresylic acid.

3. A process of removing from oil and gas wells and from petroleum pipe lines deposits which include asphaltenes and wax and which are substantially devoid of readily petroleum-soluble materials, comprising: exposing said deposits to the solvent action of a mixture of about two parts by volume of gasoline and about one part by volume of acetone.

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