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DEGREASING PROCESS

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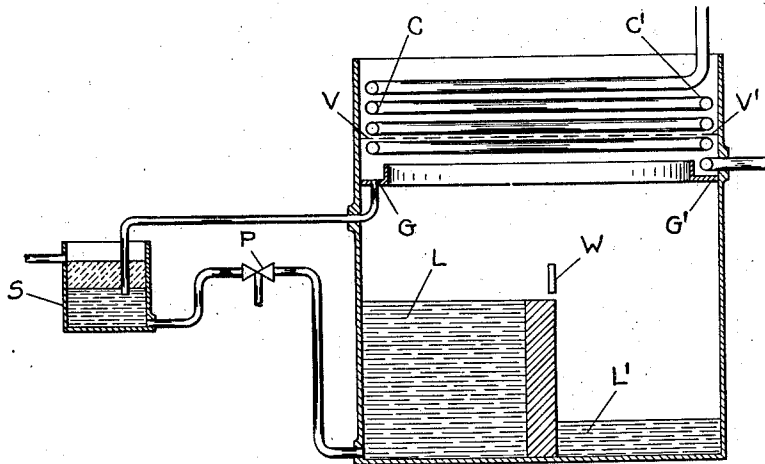


FIG. 1

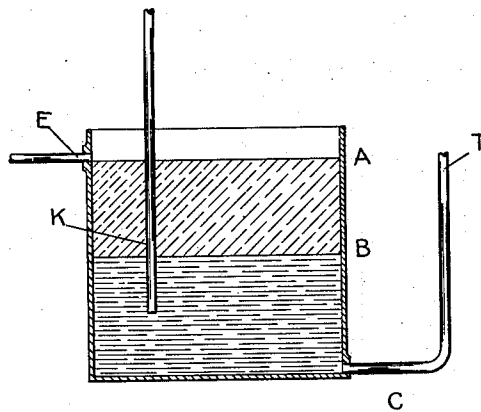


FIG. 2

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UNITED STATES PATENT OFFICE

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DEGREASING PROCESS

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This invention relates to a process of cleaning and/or degreasing materials by means of volatile solvents.

One of the objects of the invention is to provide a process for the treatment of materials with water-immiscible solvents in the presence of water.

Another object of the invention is to provide a process for the cleaning and/or degreasing of materials in the presence of a water emulsion by means of a water-immiscible solvent containing an agent which facilitates the dispersion of the emulsion in the solvent.

A further object of the invention is to provide a process for the cleaning and/or degreasing of materials in the presence of water emulsion by means of a volatile solvent containing an agent which will assist in the dispersion of the water emulsion in the solvent and which can subsequently be recovered with the solvent when this is reclaimed by distillation for re-use.

A particular object of the invention is to provide a process for the removal of oil-water emulsions from metal parts by means of a volatile solvent containing an agent which facilitates the wetting-off and dispersion of the oil-water emulsions in the solvent and a still more particular object is to provide a process for the removal of solubilized mineral, vegetable and animal oil-water emulsions from articles such as, for example, screwed, threaded or otherwise machined metal parts by means of a volatile solvent to which has been added an agent, itself substantially insoluble in water, but which renders the solvent miscible with oil-water emulsions and for the continuous removal of water by distillation and gravity separation and the recovery of the agent with the volatile solvent.

It has been proposed to clean or degrease materials or articles by treating the same with a liquid grease solvent, by immersing the materials or articles successively in one or more baths of hot or cold solvent and then in nearly saturated solvent vapor, or by treating in solvent vapor alone and finally removing from the vapor in a hot and substantially grease- or oil-free condition.

Where it is required to remove only oils or grease, this is a particularly advantageous process provided such oils or grease are completely soluble in the solvent used. However, in the presence of water, such for instance as when soap solutions are added or when such oils or grease comprise certain types of lubricant, such as those used in stamping, cutting, threading, etc., of metal parts, which consist of emulsions in water of mineral, vegetable or animal oils, solubilized by sulphonation, etc., or of soaps of alkalis or alkaline earths combined with oil, this process is not effective.

Owing to the relative immiscibility of water in the volatile solvent, the removal of such water-oil emulsions is inadequate and particularly is this the case with metal parts where these parts are required subsequently to be galvanized, plated or otherwise coated. This failure is due to the inability of the solvent to wet the interfacial surfaces between the emulsion and the material or to hold the mechanically removed emulsion in dispersion.

In using solvents which are immiscible with water, it is, therefore, frequently desirable to effect the dispersion of water or water solutions or emulsions in the solvent and this is accomplished by the addition of one or more substances to the water and/or solvent phase prior to or during use. Such substances or "addition agents" as they are called throughout the description of the present invention, have the effect of lowering the surface tension of water against solvent.

As examples of such "addition agents" reference may be made to aliphatic alcohols such as ethyl alcohol or to ethers such as dimethyl ether and ethylene glycol-monobutyl ether when added to water and a hydrocarbon solvent such as petroleum fractions or a chlorinated hydrocarbon solvent such as trichlorethylene.

Similarly "addition agents" with wetting and dispersing powers (and often other detergent properties) may be added to aqueous solutions to effect the lowering of interfacial tension between oil and water in order to facilitate the wetting of oily surfaces and the dispersion of the oil in the water solution of dispersing agent.

Examples of this class of "addition agents" are soaps of fatty acids and inorganic or organic bases, such as palmitates, stearates or oleates of inorganic alkalies such as caustic soda, caustic potash, ammonium or organic bases, such as triethanolamines and triethylamines and also sulphonated fatty oils such as sulphonated castor oil or cod oil; sulphonated fatty acids such as Turkey red oil (or sulphonated oleic acid); or sulphated higher alcohols such as the sulphuric ester of cetyl or lauryl alcohol. The soap or soap-like body may be contained in the aqueous phase or formed in situ by the neutralization of the fatty acid or fatty oil with an inorganic or organic base.

Frequently it is desirable to combine these two classes of addition agents. For example:

I. The addition of a water-soap mixture to a solvent which is immiscible with water in order to combine the specific detergent action of soap (i. e., emulsification, deflocculation) with solvent action and also as a means of bringing water to dissolve water-borne stains on textile fabrics.

II. The removal of water-oil emulsions con-

taining soap or soap-like bodies from absorbent or non-absorbent surfaces by means of solvents.

In such cases, the addition agents which are effective in the first class, i. e., for rendering water and solvent miscible, are also effective in dispersing the water-oil emulsion containing soap or soap-like bodies, in pure solvent. Thus alcohol will assist in the dispersion of an aqueous solution of soap in trichlorethylene. Alternately, the dispersion may be effected by adding an aqueous solution of a base to a fatty acid solution in solvent.

I have now found a third class of addition agent which possesses certain improved properties in effecting such dispersions. These addition agents, while soluble in the solvents employed are substantially insoluble in water and while not, themselves, capable of dispersing water in solvent, greatly facilitate the dispersion of oil and water in solvent media in the presence of soap or soap-like materials. Preferably they are volatile with the solvent.

These properties result in important advantages in the process of cleaning and/or degreasing in that when the solvent is removed from the material to be cleaned, as by distillation, solvent, water and volatile addition agent are removed from the soap and impurities and the water and solvent readily separate in the standard form of gravity separator, the addition agent, being soluble in the solvent medium, returning to the system with the solvent for re-use, while the water is rejected.

Such addition agents are cyclohexanol, methyl cyclohexanol, tetralin and their mixtures, and homologues of these substances or their mixtures.

Such agents have been used as an addition to soap for use in textile cleaning but hitherto, so far as I am aware, no system has been proposed for adding them to solvent media for the purpose of aiding the action of aqueous soap in scouring textiles and subsequently ensuring their recovery; or as a means of wetting and dispersing oil-water emulsions when these are required to be removed from non-absorbent surfaces in solvent degreasing operations.

I have found them particularly advantageous for these purposes because of their substantial immiscibility with water alone; their power of assisting detergent action in the presence of emulsifying agents, their volatility, their relative insolubility in water, their non-inflammability and relative non-toxicity.

The present invention contemplates (a) a method of making water emulsified with soap, oil or grease, miscible with the solvent used (b) the production of a homogeneous mixture of the solvent and the water emulsion (c) the relatively stable emulsion of water, solvent and an emulsifiable oil (d) the provision of an addition agent which, added to the solvent, will render the solvent and oil-water emulsion miscible thus permitting wetting and dispersion of the emulsion in the solvent.

In the preferred form of carrying out the process of the invention, the use is contemplated of a device which will permit the continuous removal of the water from the system without appreciable loss of addition agent, and the maintenance of a concentration of addition agent in liquid and vapor phases of the solvent between the limits necessary for effective working of the process.

These objects are accomplished by adding to

the solvent an agent which is soluble therein, which renders the solvent capable of forming relatively homogeneous emulsions which compositions comprising water and oil or water and grease emulsified in the presence of soap or soap-like bodies. Preferably the addition agent possesses an appreciable vapor pressure at the boiling point of the solvent used but is itself relatively insoluble and non-dispersable in water alone since this property facilitates its separation from the water removed with the solvent vapor as more fully described hereinafter.

As solvents, I employ such degreasing agents as trichlorethylene, perchlorethylene, carbon tetrachloride or other chlorinated aliphatic hydrocarbons with which I preferably admix agents comprised in the groups designated as hydrogenated cyclic hydrocarbons and hydrogenated phenols, either singly or in admixture, one with another.

Typical commercially available representatives of these groups are:

Cyclohexanol ("Hexalin") or hexahydrophenol $C_6H_{11}OH$.

Methylcyclohexanol ("Methyl Hexalin") or hexahydrocresol $C_6H_{10}CH_2OH$.

Tetrahydronaphthalene ("Tetralin") $C_{10}H_{12}$.

Hexalin and Methyl Hexalin are liquids only slightly soluble in water but miscible in all proportions with organic solvents. They are widely used in industry as stabilizers, solubilizers and homogenizers. They possess the property, although insoluble in water, of producing when combined with soap or soap-like bodies such as sulphonated oils, compositions which aid in the dispersion of aqueous solutions in solvents or solvent solutions which are immiscible with water alone.

Hexalin boils at $320^{\circ} F$. and Methyl Hexalin at $338-374^{\circ} F$. Their vapour pressures are relatively close (5% and 4% respectively, at the boiling point of their mixtures with trichlorethylene).

Tetralin is insoluble in water and soluble in practically all organic solvents. Its solvent properties for certain waxes, gums, resins and oils are superior to most solvents being used at the present time and it therefore enhances the properties of the solvent used. For use in conjunction with soaps and similar bodies it is often combined with Hexalin and Methyl Hexalin. Its vapour pressure at $90^{\circ} C$. is 2.5% of that of trichlorethylene.

One of the valuable characteristics of Tetralin, Hexalin and Methyl Hexalin is that they are solvents for soaps of the alkaline earths and therefore, assist in the removal of these bodies when encountered on materials or articles alone or in combination with oils, fats, etc., such as is the case with metal articles which have been spun or drawn with the aid of such soaps or combinations of such soaps with oils or fats.

In the preferred modification, the limiting conditions for any addition agent with any given solvent is that the partial pressure of the addition agent at the boiling point of the solvent shall be not less than the minimum concentration of the addition agent necessary for effective working of the process.

For example, the vapour pressure of cyclohexanol at the boiling point of trichlorethylene is 41 mm. mercury pressure which corresponds to a partial pressure in the vapour of the mixture of approximately 5 per cent.

(Owing to its varying content of ortho, meta, 75

and para isomers, the partial pressure of methylcyclohexanol is between 4 and 5%. That of tetrahydronaphthalene is 2.5%).

Therefore, the maximum concentration of cyclohexanol in trichlorethylene that can be kept in circulation is 5 per cent. The vapour pressure of cyclohexanol at the boiling point of perchlorethylene is 190 mm. mercury pressure, which corresponds to a partial pressure in the vapour of 25 per cent. Therefore, the maximum concentration of cyclohexanol in perchlorethylene that can be kept in circulation is 25 per cent.

The percentage of the addition agent necessary is determined by the type of water-oil emulsion to be removed, and the total amount to be dispersed at a given time in a given volume of solvent.

For normal working conditions the concentration of cyclohexanol may vary between 0.5 per cent and 5 per cent of the trichlorethylene in use.

My invention is particularly applicable for use in connection with a solvent degreaser as described in Canadian Patents 334,517, 343,743 and 343,746 employing trichlorethylene or other suitable solvent.

The articles are immersed in the liquid solvent which is agitated by boiling, for a time sufficient to attain the desired cleaning, and are subsequently treated in the vapour of the solvent.

When the articles have attained the temperature of the solvent vapour, they are withdrawn in a substantially oil-free condition. Any water originally present on the work and removed in the degreasing process as herein described, distills continuously with the solvent vapor and is condensed in the manner described in the above patents, to form a heterogeneous mixture of water and solvent.

In the accompanying drawing, Fig. 1 represents in elevation a typical vapour-liquid solvent degreasing equipment for use when water is present.

Solvent, addition agent and water boil in L and L', vapours rise to V V', are condensed on coils C and C', collected in gutter G and G', freed of water in separator S, and flow via the three-way cock P to the bottom of the compartment L, whereby liquor is displaced upwards over weir W into L', carrying oil, dirt, addition agent and water. Solvent, addition agent and water are evaporated in L' and are recirculated by condensation as above. Liquor in L and vapour in L' are the sections defined as "working zones" below.

After a short period of operation, the concentration of addition agent in the combined vapour and liquor working zones reaches a constant figure determined by whether the concentration of addition agent is initially

(1) Higher than the percentage vapour pressure of the addition agent. In this case the concentration in the working zones (excluding liquor in L') reaches a constant figure equal to the percentage vapour pressure of the addition agent at the boiling point of the mixture, and excess of addition agent collects in L'.

(2) Lower than the percentage vapour pressure of the addition agent. In this case the concentration in the working zones equals the percentage of addition agent in the total solvent present (including liquor in L').

For continuous working, the concentration of addition agent in the work zones can, therefore, be varied as required from zero up to a maximum determined by the vapour pressure of the addition agent at the boiling point of the mixture, and within these limits can be maintained at any figure desired. For certain working conditions,

however, the concentration of addition agent in L may be temporarily increased from the above maximum up to the solubility limit, the concentration reverting to the above maximum (approximately 5% for cyclohexanol) by continuous working.

Fig. 2 illustrates a typical water separator for liquids heavier than water. Water, solvent and addition agent enter at K. Water is removed at E, and solvent and addition agent at T. The water level E and the solvent level T are arranged so that a difference in head may be maintained between the water-solvent column (AC) and solvent column (TC) without accumulating so much water, that it is entrained in the solvent leaving by T. The position of the inlet K is arranged below the water surface in such a position as to allow of separation of solvent by gravity before the water leaves at E. Addition agent is contained in solvent leaving by T; and water leaving by E is substantially free of solvent and addition agent.

As the water solvent partition co-efficient of the addition agent is low and the proportion of water to solvent small in the condensate, the addition agent is substantially contained in the solvent layer and is, therefore, continuously returned to the system.

In the preferred form of my invention I use trichlorethylene in conjunction with cyclohexanol for the reason that trichlorethylene has certain preferred properties for metal degreasing and cyclohexanol, in addition to being readily available commercially and exerting an appreciable vapour pressure at the boiling point of trichlorethylene, is also relatively insoluble in water. This property of insolubility is advantageous in that it enables the addition agent to be readily separated from the water contained in the condensed vapour.

The following examples illustrate results obtained according to the invention:

Example 1

Metal parts (threaded nuts and bolts) were heavily coated with emulsion by dipping into a 30 per cent solution of sulphurized mineral oil in water and transferred directly to a boiling solution of three per cent of cyclohexanol in trichlorethylene, contained in a degreasing apparatus not fitted with a water separator. After a short immersion, sufficient to wet off the water-oil emulsion, the metal parts were removed from the liquor into the vapour and allowed to attain the temperature of the vapour before being removed from the degreaser. It was found that the water-oil emulsion was completely removed from all parts.

The process was repeated until the cyclohexanol-treated bath showed signs of reaching saturation, as evidenced by failure to completely remove water-oil emulsion without considerable agitation. At this point 750 lbs. of metal had been treated and 125 ounces of water-oil emulsion removed per pound of cyclohexanol, and although the water was not removed from the system, no appreciable separation occurred at the solvent surface.

When a water separator was included in the condensate return circuit, one per cent of cyclohexanol sufficed, the above saturation with oil-water emulsion was not reached and the continuity of the process was limited only by the periodical necessity for cleaning out the equipment as normally required.

Example 2

Perchloroethylene was used as the solvent in place of trichloroethylene in Example 1 and similar results were obtained.

For comparative purposes a similar weight of nuts and bolts prepared and treated under similar conditions were cleaned in untreated trichloroethylene. It was found that considerable amounts of emulsion were retained, especially in the threading. After 750 lbs. of metal has been treated, at this point, the whole of the water emulsion was substantially separated on the surface of the solvent.

The above examples illustrate the efficiency of my invention under conditions where articles are coated with excess of emulsified oils. In normal operations, lower concentrations of soluble oil are used than 30% and the work is drained and often considerably dried out before cleaning.

The above process is applicable to two and three liquor-compartment degreasers.

When the quantity of water-oil emulsion contained in the work is small and no solid dirt is present, a single vapor type degreaser suffices for its removal. For this purpose I prefer to use a solvent having a higher boiling point and similar or higher latent heat of evaporation and therefore, yielding a heavier condensation such as perchloroethylene with an addition agent having appreciable vapor pressure at the boiling point of the mixture in order to ensure an appreciable concentration of addition agent in the vapor. Perchloroethylene and cyclohexanol meet this requirement.

This invention facilitates the thorough removal of solvent-soluble water-containing impurities and is especially applicable to the treatment of metal parts in a solvent degreasing process where it enables the parts to be rendered so completely grease-free that they may be coated without further cleaning. Such water-bearing impurities include sulphurized and sulphonated oils and soaps of alkalies and the alkaline earths. Water-oil emulsions are rapidly removed from metal parts, particular from threaded holes and surfaces where capillary attraction and inaccessibility make the use of untreated solvent inefficient. Oil is simultaneously removed whereas heretofore it has been found that retention of water prevented access of the solvent to the oil.

Furthermore, oil-water emulsions removed from the metal surfaces or surfaces cleaned is retained in dispersion and the tendency of the water to separate at the surface of the solvent is eliminated. Prior to the application of my invention even though the water-oil emulsion was removed from the metal surface by violent boiling and/or agitation, owing to its immiscibility and lower specific gravity, it immediately separated on the surface of the solvent and contaminated the work withdrawn through it.

As many apparently widely different embodiments of my invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. Process for degreasing and simultaneously removing aqueous emulsions of soap or soap-like bodies from metal parts which comprises treating said metal parts with a water-immiscible, volatile organic solvent in the presence of a volatile material which is substantially insoluble in water but soluble in the solvent and which facilitates the dispersion of the water emulsion in the solvent, removing water, volatile material and solvent by distillation, condensing the distilled vapors, stratifying the condensate into a water layer and a solvent layer, the latter containing the predominate proportion of the volatile material and returning volatile material and solvent to the system.

2. Process for degreasing and simultaneously removing aqueous emulsions of soap or soap-like bodies from metal parts which comprises treating said metal parts with a water-immiscible volatile organic solvent in the presence of a material which is substantially insoluble in water, soluble in the solvent and has an appreciable vapor pressure at the boiling point of the solvent and which facilitates the dispersion of the water emulsion in the solvent, removing water, volatile material and solvent by distillation, condensing the distilled vapors, stratifying the condensate into a water layer and a solvent layer, the latter containing the predominate proportion of the volatile material and returning volatile material and solvent to the system.

3. Process for degreasing and simultaneously removing aqueous emulsions of soap or soap-like bodies from metal parts which comprises treating said metal parts with a water-immiscible volatile organic solvent containing a material which is substantially insoluble in water, soluble in the solvent and has an appreciable vapor pressure at the boiling point of the solvent and which facilitates the dispersion of the water emulsion in the solvent, the proportion of material to solvent being not greater than the partial pressure of the material at the boiling point of the mixture of material and solvent, removing water, volatile material and solvent by distillation, condensing the distilled vapors, stratifying the condensate into a water layer and a solvent layer, the latter containing the predominate proportion of the volatile material and returning volatile material and solvent to the system.

4. Process for degreasing and simultaneously removing solubilized mineral, vegetable or animal-oil-water emulsions from metal parts which comprises treating said metal parts with trichloroethylene in the presence of cyclohexanol, removing water, cyclohexanol and trichloroethylene by distillation, condensing the distilled vapors, stratifying the condensate into a water layer and a trichloroethylene layer, the latter containing the predominate proportion of the cyclohexanol, and returning the cyclohexanol and trichloroethylene to the system.

5. Process for degreasing and simultaneously removing emulsions of solubilized mineral, vegetable or animal oil and water from metal parts which comprises treating said metal parts with trichloroethylene containing between about 0.5 per cent and 5.0 per cent of cyclohexanol, removing water, cyclohexanol and trichloroethylene by distillation, condensing the distilled vapors, stratifying the condensate into a water layer and a trichloroethylene layer, the latter containing the predominate proportion of the cyclohexanol, and returning the cyclohexanol and trichloroethylene to the system.

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