Jan. 22, 1952 C. A. CAMPBELL 2,583,165

CLEANING COMPOSITION

Filed Dec. 30, 1948

Fig. 1.

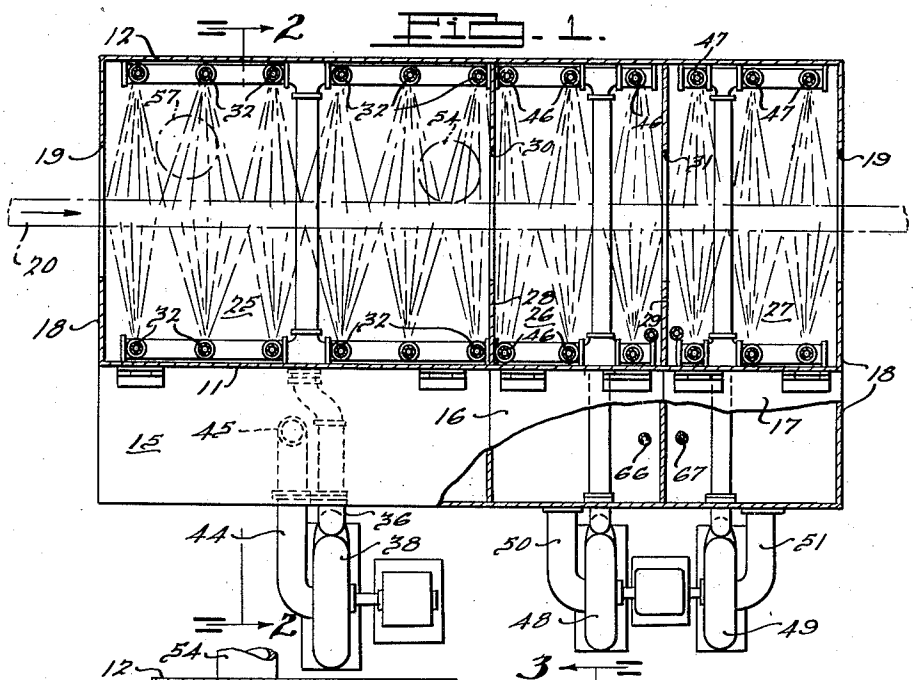


Fig. 2.

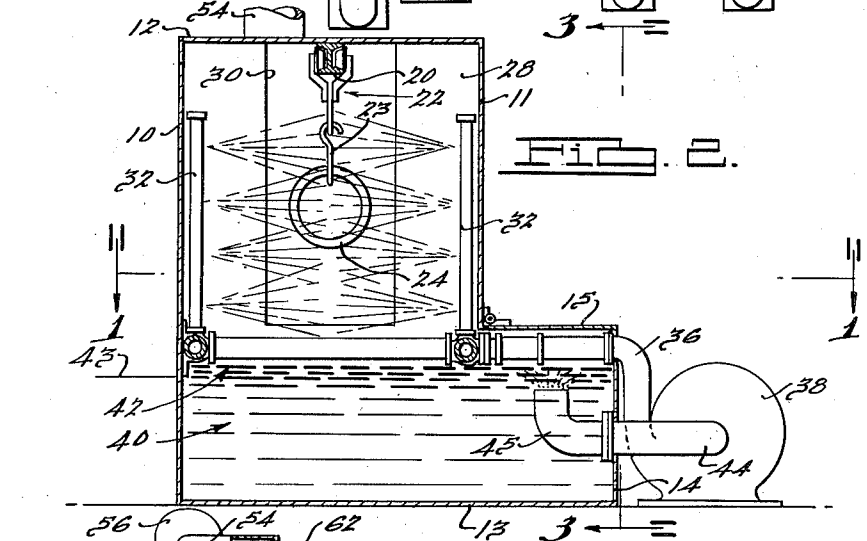
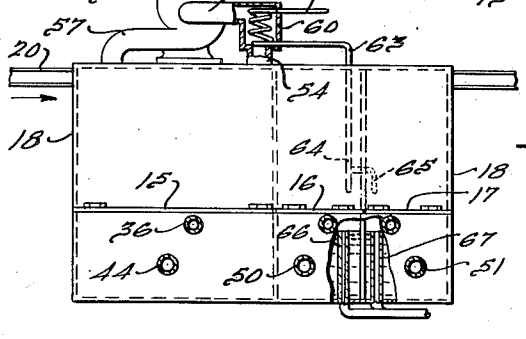


Fig. 3.



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CLEANING COMPOSITION

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13 Claims. (Cl. 252—118)

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The present invention relates to cleaning materials, and particularly such as are applicable to the cleaning of metal parts in the process of manufacture in order to prepare their surfaces for such operations as plating, rust-proofing, painting, or the inspection of the parts for minute surface imperfections, and this application is a continuation in part of applicant's copending applications Serial No. 463,495, filed October 27, 1942, now abandoned, and No. 592,522, filed May 7, 1945, now abandoned, the former being a continuation in part of applicant's application Serial No. 347,929, filed July 27, 1940, now Patent No. 2,399,205.

Metal parts in the course of ordinary manfacturing operations become coated with cutting oils, drawing and buffing compounds, mineral oil, dust, carbon smut, chips and other materials which must be entirely removed in order to prepare the surface for subsequent treatment or for certain inspection operations. It is required that the surface of the metal be perfectly clean and free from objectionable foreign material, and in the case of active metals it is essential to leave the surface in a neutral condition in order to inhibit rust, corrosion or oxidation in the interval between operations, including, in some instances, a storage interval.

Some types of material which must be removed, such as light cutting oils, are not difficult to remove with conventional cleaning baths, but serious difficulties have been encountered by reason of the fact that various cleaning methods used in the past have left the surface of the metal part in such condition that it rusts or corrodes very rapidly following the cleaning operation. Other materials, and in particular drawing and buffing compounds, are more difficult to remove. Buffing compounds contain inert materials including finely divided emery or other abrasives and also other saponifiable and semi-saponifiable stearates, greases and sometimes mineral oils. Drawing compounds contain soaps, partially saponifiable oils, saponifiable oils and fatty acid, degraws, pigments and sometimes rosin oil and, in addition, there is usually found upon the surface of the parts mineral oil, dust, carbon smut and other types of inert material which strongly adhere to the surface but must, nevertheless, be removed.

In the past, four principal classes of cleaning materials have been employed for cleaning metal parts in production; namely, alkali compounds in water, chlorinated hydrocarbons, such as trichlorethylene, ordinary hydrocarbon solvents,

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and solvent emulsions. Alkali compounds, while widely used in spray and dip cleaning to remove certain types of light soil, are not effective in removing stubborn deposits such, for example, as buffing or drawing compounds. Moreover, when used on steel they leave the surface in such a condition that it tends to rust rapidly following the cleaning operation and there is a tendency of the alkali to react chemically with the metal, particularly in the case of active metals, such as zinc die castings. Trochlorethylene and similar chlorinated hydrocarbons are most effective when used in the vapor stage, and are extensively so used. However, the solvent vapors are often noxious, even poisonous, and while they dissolve the greases and oils they will not entirely carry off inert materials and soaps. Therefore, it is often necessary to hand-wipe parts which have been subject to vapor solvent cleaning. Again it is found that the surface is left in such a condition that the parts tend to rust. Ordinary hydrocarbon solvents have been used to a limited extent in dip or spray cleaning, usually while hot. They are effective in dissolving greases and oils, but have no effect on most soaps; they are unable to carry inert or nonsoluble materials in suspension, and they create a fire hazard. These, too, leave the parts in a condition in which they rust rapidly. Stable solvent emulsions are used to a limited extent for cleaning by dip methods, but are not particularly effective in the removal of oils and greases. If heated or sprayed, they tend to foam; and if heated, much of the solvent is lost by evaporation.

It is the general object of the present invention to provide highly effective inexpensive methods, materials and apparatus for conducting cleaning operations of the type mentioned without the disadvantages of the prior practice.

Another object of the invention is to provide a single cleaning bath which, when used either as a spray or dip bath or both, will effectively remove oils, fatty acids, soaps, greases and inert materials without reacting with the metal part being cleaned and which will leave the surface of the part in a condition such that it will not rust within a reasonable period under ordinary storage conditions, but on which surface there is no visible film.

Another object of the present invention is to provide a novel form of cleaning bath comprising an unstable mixture of a cleaning solvent and a solvent-water emulsion, which bath may be used in either spray or dip methods of cleaning, and

which may be re-used repeatedly for a relatively long period.

Another object of the present invention is to provide a novel cleaning solution for use in preparing cleaning baths of the type mentioned.

Other objects, which include the provision of apparatus designed to carry out the cleaning operation in the best possible manner, including the provision of means for limiting loss of cleaning solution by evaporation, will become apparent from the following specification, the accompanying drawings, and the appended claims.

In the drawings, in which like numerals are used to indicate like parts in the several views throughout:

Figure 1 shows a horizontal section, taken on the line 1—1 of Figure 2, of a spray washing machine of a type adapted for use in accordance with one phase of the present invention;

Figure 2 shows a vertical section of the same machine taken on the line 2—2 of Figure 1; and,

Figure 3 is a side view on a reduced scale, taken on the line 3—3 of Figure 2, parts being broken away to show a portion of the interior of the machine.

In accordance with the present invention, metal parts are cleaned by subjecting them to the action of an unstable mixture of a cleaning solvent emulsion and an unemulsified cleaning solvent, which unstable mixture is referred to throughout this specification as the bath, or cleaning bath. This bath is made up of a solvent emulsion containing any suitable cleaning solvent, water, and an emulsifying agent such as a water soluble soap. This portion of the bath, which is referred to throughout as the emulsion, is a stable solvent in water emulsion having the property of being able to clean by wetting action and dispersion. The cleaning bath, in addition to the cleaning emulsion, contains solvent in an amount greater than can be emulsified with the cleaning emulsion, with the result that the additional solvent remains separate from the emulsion and tends to float on the surface of the bath in a layer.

The cleaning bath of the present invention may be used for cleaning either by the dip or spray method, but is most advantageously used in spray cleaning.

In the dip method of cleaning, the parts to be cleaned are simply dipped into the material, which is preferably maintained during dip cleaning at a temperature in the order of 160° to 180° F. The parts to be cleaned, when dipped into the bath, first enter and then pass through the solvent layer at the top before entering the emulsion beneath the solvent layer. This exposes the material to be removed from the part to the action of the solvent first. When this material contains greasy and oily substances, as well as inert particles, the solvent penetrates the material to be removed, wets or coats the inert constituents thereof and acts generally to soften the grease and oily matter in the material. As the part moves into the cleaning emulsion, in which it is preferably held for a short period depending upon the amount of material which must be removed, the emulsion causes a further wetting, emulsifying and softening of the material and also tends to cause a dispersion of the material on the surface of the part and in the cleaning emulsion thus loosening it and spreading it to a condition in which it will be readily removed in subsequent rinsing operations. Then, as the part is removed from the bath out through the solvent layer for a second time, the penetrating and softening action of the solvent is repeated and, in addition, the mechanical movement of the solvent over the work causes a partial or complete removal of the loosened, softened and dispersed material originally upon the part to be cleaned. The penetrating and wetting properties of the solvent being superior to those of the emulsion cause an initial penetration and coating by the solvent that facilitates subsequent penetration and dispersion by the emulsion.

If the dip method of cleaning is used alone, as soon as the part is removed from the cleaning bath it should be subject to a rinsing operation, preferably in the form of a water spray which will mechanically remove and wash away any remaining vestige of foreign material and the cleaning bath. The free solvent in the bath greatly facilitates rinsing, apparently because the free solvent and emulsion, being dispersed throughout the material on the surface, make it easier to break and wash away the material than would be the case if it were either pure solvent or all a stable emulsion. At the same time, the emulsion blankets and prevents drying out of the solvent between the washing operation and the rinsing operation and serves as a carrier for inert materials and solvent. As a result, the metal part is very readily rinsed to a free, clean surface, upon which no trace of foreign material can be seen and which, additionally, is sufficiently clean chemically to take electroplating or rust-proofing treatments successfully.

The above described cleaning bath of the present invention may also be used to excellent advantage in spray cleaning, in which event it is mechanically mixed in any suitable manner and sprayed directly upon the work to be cleaned by any suitable spray nozzle.

A machine suitable for carrying out the spray cleaning process is illustrated in the drawings. As there shown, the machine comprises a sheet metal casing of any desired construction having side walls 10 and 11, top wall 12, and bottom wall 13. The lower portion of the casing has a projection at one side defined by an auxiliary side wall 14 spaced outwardly from the wall 11 at the upper part of the machine on the same side. The offset between the walls 11 and 14 is closed by a plurality of hinged lids 15, 16 and 17. The ends of the machine are partially closed by end walls 18, which are entirely closed at their lower portions but have at their upper central portions openings 19 through which the work to be cleaned is passed.

Any desired means for conveying the work through the machine may be utilized, but, as shown in the drawings, it is preferred to utilize a chain type of conveyor which runs upon an I-beam track 20 extending entirely through the machine and the openings 19 in the end walls 18 thereof. The chain conveyer, indicated generally at 22, is provided with a plurality of longitudinally spaced hooks 23 for supporting the work 24 to be cleaned.

The machine is divided into three compartments, 25, 26 and 27. The compartment 25 is the washing compartment. Compartment 26, which is the first rinsing stage, is separated from compartment 25 by a wall 28. Compartment 26, in turn, is separated from compartment 27, the second rinsing stage, by means of a wall 29 similar to the wall 28. The walls 28 and 29 have openings 30 and 31 therein, which openings are similar to the openings 19 in the end walls 18.

The lower portions of the compartments 25, 26 and 27, which are separated from each other by the lower portions of the walls 28 and 29, form reservoirs for retaining the washing fluid and rinse water, respectively. That is, the lower portion of the compartment 25 forms a reservoir for the washing fluid while the lower portions of compartments 26 and 27 form separate reservoirs for rinse water.

Mounted in the compartment 25 adjacent the side walls 11 and 12 are a plurality of vertically extending spray pipes 32 connected by suitable piping to the discharge outlet 36 of a pump 38. The vertically extending spray pipes are provided throughout their length with a plurality of spaced nozzles of any desired form, such as milled slots in the pipe, adapted to spray the cleaning material upon the work carried by the chain conveyor 22. It will be noted that the last spray pipes are positioned very close to the wall 28, with the result that the wall 28 forms a baffle acting to prevent the cleaning fluid from entering the first rinsing compartment.

The cleaning material which is discharged by the spray pipes 32 falls back into the reservoir in the bottom of the spray compartment 25 and means are provided for drawing the cleaning material from this reservoir and conducting it to the intake of the pump 38. It will be noted, as shown in Figure 2 of the drawing, that the cleaning bath in the reservoir comprises an underlying body of emulsion indicated 40 upon the top of which is a layer 42 of unemulsified solvent. These two immiscible liquids have a distinct interface, the level of which is indicated by the line 43 in Figure 2. It is necessary, in order to properly conduct the washing operation, to draw into pump 38 a mixture of these two immiscible fluids and this is accomplished in the machine illustrated in the drawings by connecting the pump intake 44 to a pipe 45, the open end of which extends vertically and lies just below the interface 43 of the two liquids. As a result of this arrangement, the pump suction draws in part upon the solvent layer 42 and in part from the underlying emulsion layer 40, thus drawing in a mechanical mixture of the two immiscible liquids. The action of the pump, as well as the turbulence created by the spray, renders this mechanical mixture an exceedingly intimate one, with the result that the free or unemulsified solvent is thoroughly dispersed through the spray.

Aside from the simplicity of this method of mixing the two layers, the method has the further advantage that the relative proportions of the two liquids may be readily varied in any given installation by varying the distance between the top of pipe 45 and the interface 43, or, in other words, by adjusting the level of the interface. This may be done readily, since the system is a closed one, by varying the quantity and proportions of the cleaning bath in the reservoir.

The ratio of the amounts of the two liquids, which are drawn into the pump, is a function of the pump capacity, the intake pipe diameter, and the distance between the top of the pipe and the interface. These three factors may, of course, be adjusted to produce any desired ratio. Excellent results in the removal of buffing compounds from zinc die castings in preparation for electro-plating have been secured in an installation in which the pump capacity was 500 gallons per minute, the intake pipe diameter was four inches, and the distance between the top of the pipe and the interface was from four to six inches. It is, of course, necessary to make additions to the bath from time to time to compensate for evaporation loss and drag out which otherwise might vary the level of the interface.

In removing cutting oils and such materials which are more readily removed from the work than buffing and drawing compounds, it has been found desirable where the parts are to be painted to locate the intake pipe at a point further removed from the interface between the unemulsified solvent and the solvent emulsion in order to draw into the spray a smaller proportion of unemulsified solvent since this leaves the surface of the parts in a better condition for paint adherence. Accordingly, in such case less solvent is used in the bath and the pump intake pipe extends horizontally into the tank at a point about thirty inches below the interface. It is essential, however, even in such cases to maintain the unemulsified solvent layer on the bath. There is sufficient turbulence created by the spray and the circulation of the fluid to carry a certain proportion of the desired free solvent into the underlying emulsified layer and thence into the pump.

When chips are being removed from the work, it is desirable to employ a screen on the intake pipe.

Following the cleaning spray, the parts are either subject to an air blow off or to a rinsing operation. In many cases a water rinse is unnecessary, it being sufficient simply to subject the parts to a blast of compressed air to remove all traces of the bath. This is due to the fact that the cleaned metal surface sheds the cleaning material and water readily. Ordinarily only a few drops remain on the surface and they are bodily removed by the air blast rather than dried on the surface. In removing buffing compounds from zinc die castings, it has been found preferable to subject the parts to a water rinse and, accordingly, in the apparatus illustrated in the drawings two rinsing stages are provided.

The two rinsing stages 26 and 27 are identical and each comprises a plurality of vertical rinsing spray pipes 46 and 47, respectively, connected by suitable piping to the discharge side of individual pumps 48 and 49, respectively. The pump inlets 50 and 51 are connected directly to the rinse water reservoirs in the lower parts of compartments 26 and 27, so that the rinse water is recirculated. Recirculation of the rinse water is desirable not only because it results in a saving of water, but also a saving of heat since the water is sprayed at the preferred temperature of 120° F. It will be noted that the last washing sprays 32 are positioned quite close to the first rinsing sprays 46, being separated only by the wall or partition 28. This is desirable in order to avoid any drying off of the parts between the last washing spray and the first rinsing spray.

The cleaning bath in the reservoir of compartment 25, as well as the rinse water in the reservoir of compartments 26 and 27, is maintained at the desired temperature, preferably 120° F. to 160° F., by any suitable means such as thermostatically controlled steam coils, not shown, in the bottoms of the reservoirs.

In order to avoid contamination of the rinse water by the vapor from the washing spray and for the further purpose of preventing loss of cleaning material due to evaporation, there is provided a circulating and condensing system shown best in Figure 3. As there shown, there is provided an air conduit 54 leading from the

top of the machine casing at a point on the washing compartment side of partition 28, as shown in dotted lines in Figure 1. The conduit 54 leads to the intake of a fan 56, which discharges into a conduit 57 leading back into the top of the casing at a point just inside of the entering end wall 18, also shown in dotted lines in Figure 1. By withdrawing air and vapor from a point adjacent to but on the washing compartment side of the opening 30 in partition 28, a flow of air from the rinsing compartment into the washing compartment is created, which is effective to prevent entry of the vapor from the washing spray to the rinsing compartments. By leading the vapor and air back through the discharge conduit 57 into the opposite end of the washing compartment, any of the vapor which has condensed will be returned to the cleaning bath and a certain amount of the uncondensed vapor, if any, when coming in contact with the washing spray, will likewise be condensed. A portion of the balance may flow outwardly through the opening 19 in the end wall 18, while the rest will flow toward the inlet pipe 54. By placing a condenser, shown more or less diagrammatically at 60, in the inlet pipe 54, it is possible to condense a greater portion of the vapors drawn into the pipe 54. As a result, loss of cleaning fluid is further reduced. The form of condenser shown is of the water cooled type utilizing a source of water which enters the condenser from a pipe 62 and is discharged through pipe 63. It is preferable to constantly overflow the rinse tanks in order to remove any dirt or foreign material which may collect as a scum on the surface, and, therefore, it is advantageous to run the condensing water from pipe 63 directly into the rinse water reservoirs. This may be done in any desired manner, such as that indicated by the dotted line pipes 64 and 65 in Figure 3. Suitable means, such as the two overflow pipes 66 and 67, may be provided to take the overflow from the rinse tanks.

The particular arrangement and proportions of the washing machine are not critical as it is possible to utilize a longer machine or one which is arranged in general U-shape instead of being arranged in a straight line, and any desired number and arrangement of washing and rinsing sprays may be utilized.

One advantage of the spray cleaning method is that a much more dilute bath may be used and, in addition, the material may be sprayed at a relatively low temperature. The action of the bath in spray cleaning is somewhat similar to that described in connection with the dip process, except that the various phases of the attack on the material to be removed from the parts occur more or less simultaneously; that is to say, the unemulsified solvent penetrates and softens the grease and oil constituents of the material and wets the inert constituents, while the emulsion wets, emulsifies and softens certain of the ingredients and disperses the material. The mechanical force of the spray assists the penetration, dispersion and removal of the material. However, the free solvent and the emulsion in finely divided form are intimately dispersed throughout each other at the surface of the work as a result of the mechanical agitation of the mixture. This greatly increases the cleaning efficiency. In addition, this fine dispersion of normally immiscible materials greatly reduces the effective surface tension of both with the result that the surface layer of cleaning material is quickly and entirely shed when the article is subject either to an air blow off or a water rinse.

In some cases, for example, where it is necessary to remove heavily caked buffing compounds from zinc die castings preparatory to electroplating, it is advisable to use both the dip and spray cleaning methods in succession. In this combination process, the parts to be cleaned are first dipped in the cleaning bath in the manner previously described and are then subject to a spray cleaning operation without any intermediate rinse. The spray cleaning operation should be conducted on the part before it has time to dry, although it is found that the cleaning emulsion from the dip bath tends to prevent or retard drying for a reasonable interval between the two washing operations, with the result that it is possible to have an intervening interval of several minutes.

When the cleaning bath of the present invention is used for removing ordinary buffing or drawing compounds, whether in the dip or spray process, the material removed from the parts to be cleaned gradually contaminates the cleaning bath and reduces its efficiency. The most serious contamination is caused by the soapy constituents which find their way into the cleaning bath, since they act as emulsifying agents and gradually increase the capacity of the bath to emulsify the excess solvent. Accordingly, as the baths are used continuously the excess solvent which initially floats upon the bath in a separate clear layer is gradually emulsified with the cleaning emulsion beneath, and the free solvent layer reduces in amount until eventually it entirely disappears, all of the solvent having been emulsified with the cleaning emulsion. As soon as the bath becomes a complete stable emulsion its cleaning efficiency is greatly reduced.

The period of time required for the cleaning bath to reach this completely emulsified stage depends upon the amount of cleaning which is done, the initial size of the bath, the proportion of solvent initially present and any additions made during the life of the bath, and the amount of soapy or emulsifying agents in the dirt or soil which is being removed from the parts to be cleaned. Under some extreme conditions, the bath may become completely emulsified in from four to eight hours. When this occurs, the bath should no longer be used.

It has been found that when the soil being removed contains these materials, which act as emulsifying agents, the efficiency and the useful life of the bath may, when used in the spray process, be very greatly increased by keeping the cleaning emulsion in an acid condition and controlling the acidity within certain well defined limits. Thus, in one case involving the removal of buffing compounds from zinc die castings, when sufficient acid or acid reacting salt was added to the cleaning emulsion to maintain a pH in the order of 2.0—3.5, the useful life of the bath was increased from four to thirty-two hours.

In most cases the above described acid treatment cannot be used in the dip washing method because of the fact that the acid in the cleaning emulsion will etch the metal parts in production. For some reason, not entirely understood, this etching may be eliminated in the spray washing method, even though an exceedingly chemically active metal, such as zinc, is being cleaned. Apparently this is due to a blanketing of the metal

by a film of unemulsified solvent in which there is no acid. At least, it is noted that if under any given conditions etching accurs in the acidified spray cleaning operation it can be eliminated without changing the pH either by increasing the amount of solvent in the bath or by dipping the work either in pure solvent or the regular dip bath immediately before the spray cleaning operation, or by both of these expedients. In addition, temperature plays an important part in the tendency of the acid to attack the metal, and it is noted that there is much less likelihood of acid attack at temperatures of 130° F. to 150° F., which is the preferred range when acid is used, than at higher temperatures.

The particular ingredients to be used in accordance with the cleaning methods outlined above may be widely varied, as may the proportions of the material used. These variations depend in any particular case upon the nature of the cleaning operation to be carried on and other factors. As a general guide, a number of specific examples are hereafter given, along with an indication of the factors influencing the choice of constituents as well as the relative proportions of the various ingredients.

While, as previously indicated, the cleaning emulsion is a cleaning solvent in water emulsion formed by any suitable soap or other emulsifying agent water soluble oleates are of peculiar advantage and it is preferred to use as the emulsifying agent an amine soap formed from oleic acid, since such soaps have excellent wetting and penetrating properties and, in addition, are soluble in oils which, for reasons to be pointed out hereafter, is an advantage. However, the principal advantages of the invention may be obtained with any other water soluble emulsifying agent or mixture of such agents capable of dispersing the solvent through the continuous water phase.

Water soluble emulsifying agents occur in a wide variety of chemical classes. The better known species are usually alkali metal salts or sulfonates or a combination of these because of the fact that sulfonation and salt formation tend to increase the water solubility of organic molecules. Other prominent classes include the amine soaps and certain highly oxygenated species wherein water solubility is secured, for example, by the introduction of a plurality of alkyloxy radicals into the molecule.

Although the water soluble emulsifying agent or mixture of agents to be used in the practice of the invention may be selected from any of the known classes, the following compounds and classes of compounds are typical of those contemplated.

Sodium oleate.
Potassium oleate.
Sodium stearate.
Potassium stearate.
Sodium abietate.
Potassium abietate.
Sodium tall oil soap.
Potassium tall oil soap.
Sorbitan monopalmitate polyoxy-alkylene derivative.
Sorbitan monolaurate polyoxy-alkylene derivative.
Alkyl phenoxy polyethoxy ethanol.
Sodium sulfonate.
Potassium sulfonate
Sodium naphthenate.
Potassium naphthenate.
Sodium oleyl sulfate.
Sodium lauryl sulfate.
Sodium dihydroxystearate.
Sodium cetyl sulphonate.
Sulfonated N-propyloleamide.
Alkyl O-naphthionic acid.
Sodium salt of the sulfuric ester of N-hydroxyethyldioctylamine.
Sodium salt of sulfonated stearic acid anilide.
Alkali metal salts of ethanolamine soaps with naphthenic acids.
Tetrasulfuric ester, and its sodium salt, of N, N-di(2,3-dihydroxypropyl) dodecylamine.
Sodium hexadecanesulfonate.
Sodium chloromethanesulfonate.
Sulfonated N-methyloctadecenylamine.
Sulfonated N-benzyloctadecenylamine.
Sodium allyl dodecylphenyl ether.
Sulfonated benzyl aliphatic ethers.
Sodium, potassium, ammonium, and water soluble amine soaps of stearic acid, oleic acid, rosin, tall oil, vegetable-oil fatty acids and animal-fat fatty acids.
The water soluble sulfates and sulfonates of the following classes as well as their sodium, potassium, ammonium and low molecular weight amine soaps: alkyl-aryl sulfonates, mahogany sulfonates, sulfated fatty alcohols, alkyl sulfonates, sulfonated amides, and sulfonated monoglycerides.
The water soluble polyoxyethylene ethers of fatty alcohols.
The water soluble polyoxyethylene esters of fatty acids.
The water soluble polyoxyethylene ethers of alkylated aryl compounds with between 3 and 20 ethylene oxide residues.

The solvent constituent of the solvent emulsion is preferably largely made up of the same solvent which forms the unemulsified solvent layer of the cleaning bath. To obtain the best results, the solvent should be lighter than water so that it will float on top of the emulsion. The preferred grease solvent is a refined petroleum hydrocarbon having a specific gravity in the order of .70 to .85. This range includes gasoline, mineral spirit, kerosene and mineral seal oil. The initial boiling point should not be materially less than 300° F. and the boiling range should not exceed 700° F. Best results are obtained with a refined oil (mineral spirit) having a specific gravity of about .80, a flash point of about 155° F., and a boiling range as follows:

Initial	376° F.
10%	403° F.
50%	430° F.
90%	458° F.
Top	500° F.

Other water insoluble grease solvents may be used, or mixtures of grease solvents may be employed so long as the major constituents are insoluble in water. While grease solvents which are heavier than water are less desirable, some of the advantages of the present invention may be obtained through their use. Thus, chlorinated aliphatic hydrocarbons, such as carbon tetrachloride, and chlorinated aromatic hydrocarbons, such as orthodichlorobenzene, may be employed. It will be appreciated, however, that in such case the solvent will form a layer on the bottom of the emulsion, instead of the top.

While a remarkable improvement over pre-

viously known cleaning compositions results from the unstable mixture of emulsion and unemulsified solvent regardless of the nature of the emulsifying agent employed and even though the composition contains no other ingredients than those mentioned above, nevertheless further advantages are achieved if the solvent constituent of the composition contains as a minor portion thereof (i. e., 5% to 20%) either steam distilled pine oil or a liquid terpinyl glycol ether, preferably terpinyl ethylene glycol monoether. (Terpinyl ethylene glycol monoether is not obtainable in a pure state at a reasonable cost, but a product which gives excellent results is sold commercially under the trade-name of "Terpesol No. 8" by the Hercules Powder Company. This product has the following approximate composition: terpinyl ethylene glycol monoether 64%, other terpinyl glycol ethers 16%, terpinyl methyl ethers 10% and the balance terpene hydrocarbons and alcohols.) Both pine oil and terpinyl ethylene glycol monoether have excellent solvent properties and assist in blending the other ingredients. More important, they impart a surprising increase in rust resistance to the cleaned metal and eliminate visible residues on the work which are sometimes obtained in the absence of these products when hard water is used. Of these two products the terpinyl glycol ether is perferred because of its higher boiling point.

Such grease solvents as pine oil and terpinyl ethylene glycol monoether are very effective and could be used as the only solvent in the composition except that their high cost makes that practice prohibitive from a commercial standpoint. It is for this reason that the preferred grease solvent is largely a petroleum hydrocarbon solvent with only a minor portion consisting of other hydrocarbon grease solvents such as pine oil or terpinyl ethylene glycol monoether.

In order to make available for sale and shipment a mixture of all of the ingredients (excepting water and acidifiers) necessary to carry on the process, it is preferred to combine the emulsifying agent and solvent constituents in a clear stable solution, so that no settling or layering of the material will occur prior to use. It is partly for this reason that the use of an amine soap is preferred, since soaps of this type are soluble in hydrocarbon solvents and oils to a certain extent. In addition, if necessary, a suitable coupling or blending agent such as ethylene glycol monobutyl ether or cyclohexanol may be used to help hold the remaining constituents in a stable solution. Otherwise, the material may separate at higher temperatures, i. e., above 70° F. or 80° F. The pine oil and terpinyl glycol ether act to a certain extent as blending agents.

Other blending agents may be employed in accordance with known principles in order to produce a stable soluble of the emulsifying agent in the solvent. Thus, butyl alcohol, hexylene glycol and "carbitols" such as ethyl "carbitol" may be used in place of the blending agents mentioned. Moreover, since some of the emulsifying agents are relatively insoluble in the solvent, materials which are only oil soluble but have an affinity for the emulsifying agent may be used. For example, amyl alcohol, sodium sulfonate or sodium naphthenate may be used to advantage with the sodium and potassium soaps listed above. Sorbitan monopalmitate, sorbitan monolaurate and phthalic glycerol alkyd resin may also be used as blending agents because of their high solubility in the hydrocarbon solvent and their affinity for water soluble emulsifying agents. The choice of water soluble emulsifying agents and the blending agents necessary in each case to produce a stable nonaqueous solution involves the application of known principles and, in itself, forms no part of the present invention.

A further advantage of initially preparing a concentrate of all ingredients except the water is that emulsions made by combining concentrate of all nonaqueous ingredients with water are less stable than those made by other methods. It is obvious that various proportions and ingredients may be used but, as examples, satisfactory formulae include the following:

	I.	II.
	Gal.	*Gal.*
Triethanolamine	2	2
Oleic acid	4	4
Ethylene glycol monobutyl ether	1	2
Pine oil or terpinyl ethylene glycol monoether	15	15
Petroleum hydrocarbon solvent	56	182

Each of the above mixtures of ingredients forms a clear amber solution which is permanently stable and which, therefore, is ready for addition to a suitable quantity of water for use at any time. It contains not only the solvent and emulsifying agent necessary to form the emulsion, but also the excess solvent necessary in the cleaning bath. It may be combined with any desired amount of water up to one part of solution to one hundred and fifty parts or more of water, and when so combined with water becomes an unstable mixture of the cleaning emulsion and excess solvent. A certain percentage of the solvent in the above mixture goes into the emulsion, but a substantial percentage simply remains on top of the bath as a clear unemulsified layer. The amount of solvent in the solution does not appear to be critical except that it must be more than the amount which will be emulsified by the emulsifying agent present. Laboratory experience demonstrates that the minimum quantity of the petroleum solvent which can be employed and still have a trace of unemulsified solvent in the resulting material under still tank dip cleaning conditions is approximately twice the quantity of soap present if there is no pine oil or terpinyl glycol ether in the material or approximately three times the amount of soap present if pine oil or terpinyl glycol ether is also present in proportions indicated in the above formulae. As a practical matter, it is preferred to use at least six times as much of the petroleum solvent as emulsifying agent. This would mean a minimum of thirty-six gallons of petroleum hydrocarbon solvent in the above formulae. A greater amount of solvent than that utilized in formula No. II may be employed. Thus, as much as two hundred and fifty parts of solvent may be successfully used, but in actual practice no particular advantage has been noticed when the larger quantity of solvent was employed.

The amount of solvent employed depends upon the nature of the cleaning operation, greater amounts being required for the more difficult cleaning operations. Thus, formula No. I, given above, is highly satisfactory for almost all ordinary metal cleaning operations where it is only necessary to remove cutting oils, chips and the like. Formula No. II has been employed with great success in the removal of buffing compounds from zinc die castings and the removal of lapping

compound from steel parts. The previously described acid treatment is preferably employed only in the more difficult cleaning operations, such as those in which large quantities of solvent are used.

The amount of water which should be added to the non-aqueous solutions depends upon the conditions and the type of cleaning operation being conducted. For example, in dip cleaning a much smaller quantity of water is used, satisfactory results having been secured with from eight to ten parts of water to one part of either of the above solutions. As little as four parts of water have been employed with success in dip cleaning, but the results do not appear to justify the greater, and consequently more expensive, solvent concentration.

In spray cleaning, excellent results have been secured with from thirty to fifty parts of water to one part of either of the above solutions. While that range of dilution is preferred for most purposes, in some cases greater dilution may be employed to advantage. Thus, in one case light cutting oils and chips were successfully removed in a two-stage spray cleaning machine employing three hundred parts of water to one part of formula No. I in the first stage, and one hundred and fifty parts of water to one part of formula No. I in the second stage. In this case, an air blow-off was employed following the second stage and the cleaning operation preceded painting. The high dilution ratio in this instance was found to give the best paint adherence. With such high dilution ratios, the free solvent layer becomes almost invisible, but the necessary excess solvent is nevertheless present. In spray cleaning, as little as fifteen parts of water to one part of the remaining ingredients has been employed with success, but, again, the result noted did not justify the expense of the greater concentration. When acid is employed in the emulsion, it is generally necessary to adjust the proportions of water and solvent in the cleaning spray by experiment in order to avoid etching of the metal.

When other emulsifying agents, soaps, solvents and blending agents are employed than those specifically referred to in formulae I and II, their relative proportions may vary. However, it is no problem to avoid use of too much emulsifying agent and the minimum amount required is merely a matter of choice. As a rough guide applicable to most emulsifying agents, it is found that an amount by volume in the order of one twentieth of the amount of the total solvent present is satisfactory, although that proportion may be increased to twice that value or reduced to half, depending upon the degree of emulsification desired. The only essential requirement is that a portion of the solvent in the bath remain unemulsified under the conditions of use, and it will be understood that such a bath is intended by the term "unstable" as used herein to describe the mixture of emulsion and unemulsified grease solvent. For any given combination of solvent and emulsifying agent the choice of blending agents and the determination of their amounts is a routine matter to those skilled in the art.

The use of acid or acid reacting materials in the bath forms no part of the present invention, since that phase of the herein described process is disclosed and claimed in Boleslaus J. Szatyn Patent No. 2,399,267, granted April 30, 1946. It will be understood, however, that the principles and advantages of the present invention are realized regardless of whether or not acid is employed.

The performance of compositions in accordance with the present invention is characterized by two seemingly contradictory and surprising features, namely, the remarkable cleaning efficiency and the corrosion resistance imported to the cleaned work. Hitherto, protection against rust and corrosion, even for brief periods of hours, has required visible protective films of soaps or oils which are either purposely applied or constitute residues from incomplete cleaning operations. These films, themselves, must be removed by a cleaning operation to prepare the surface for painting, plating or some inspection operations and the prior cleaning methods available left the surface subject to corrosion during subsequent handling. In contrast the cleaning compositions of the present invention not only remove practically all forms of foreign materials in a very brief time, leaving a surface on which no residue can be detected by visual inspection, but the cleaned metal resists corrosion under the most severe atmospheric conditions for periods sufficient to permit inspection, ordinary handling and even brief storage (i. e., several days) pending subsequent treatments.

Since it is known that bare steel, for example, will rust visibly in a few hours in a humid atmosphere, it is obvious that some exceedingly thin film must be left on the work. This film, however, does not interfere with paint adherence and in fact seems to enhance it. Moreover, it either does not interfere with plating operations or is removed in the preliminary dip conventionally employed or in the plating solution itself without harmful results.

Extended investigations of this phenomona have lead to the discovery that when a water soluble soap is used as the emulsifying agent the soap ionizes and a substantial part of the fatty acid concentrates in the hydrocarbon solvent while a substantial part of the alkali concentrates in the water. This, in itself, is not beneficial, but is rendered so because an unstable emulsion containing unemulsified hydrocarbon solvent, has the peculiar property of not only removing all foreign material from a metal surface, but of leaving that surface wet with the hydrocarbon solvent. The fatty acid in the solvent, being highly polar, evidently adsorbs on the surface and thus forms a protective film of near molecular thickness which protects the surface. If the emulsifying agent is not of the ionizing type, the surface is still cleaned and wet with the solvent and a film of emulsifying agent adsorbed on the surface although possibly to a lesser degree than in the case of soaps. For that reason when corrosion resistance is important, it is preferred to use either a water soluble soap or a material such as a sulphonated oil which will dissolve in the hydrocarbon and adsorb on the metal surface.

In contrast, when a metal surface having a greasy coating is cleaned in a stable emulsion there is no wetting of the metal surface with the solvent. Instead the original oil or grease film (including any suspended inert materials) is not entirely removed and soap is deposited in the residual film. The result is usually a visible film which would prevent paint from adhering and would interfere with plating.

In the appended claims, the term "emulsion" is used to refer to a stable emulsion or colloidal suspension of a water immiscible liquid in water in the presence of an emulsifying agent. The term "solvent" or "grease solvent" is used to refer to water insoluble cleaning solvent liquids adapt-

ed to dissolve greases and oils and other similar materials. The term "coupling" or "blending agent" refers to such compounds as ethylene glycol monobutyl ether, cyclohexanol, pine oil, higher alcohols and other compounds which have the property of blending soaps and oils to produce a stable solution. The expression "an unstable mixture of solvent and an emulsion of solvent in water" and similar expressions appearing in the claims designate a bath containing insufficient emulsifying agent to emulsify all of the solvent present, with the result that on standing the emulsion and excess solvent separate.

While several embodiments and examples of the present invention are given, it will be understood that changes may be made in the apparatus, methods, various ingredients and proportions without departing from the spirit of the invention or the scope of the appended claims. Where proportions are given, it will be understood that they are proportions by volume.

What is claimed is:

1. A cleaning bath for cleaning metal parts, comprising an unstable mixture of an unemulsified water insoluble grease solvent the major portion of which is a refined petroleum hydrocarbon solvent having a specific gravity of about .70 to .85, and an emulsion of said grease solvent in water, said emulsion containing as an emulsifying agent a water soluble oleate and the water being in an amount from eight to one hundred and fifty times the volume of all other ingredients.

2. A cleaning bath for cleaning metal parts, comprising an unstable mixture of an unemulsified water insoluble grease solvent and an emulsion of said grease solvent in water, said solvent containing from thirty-six to two hundred and fifty parts by volume of a refined petroleum hydrocarbon solvent having a specific gravity of about .70 to .85 and approximately fifteen parts by volume of a solvent from the group consisting of pine oil and a terpinyl ethylene glycol monoether, said water being in an amount from eight to one hundred and fifty times the volume of all other ingredients, and said emulsion containing as an emulsifying agent a water soluble oleate soap.

3. A cleaning bath for cleaning metal parts, comprising an unstable mixture of an unemulsified water insoluble grease solvent, and an emulsion of said grease solvent in water, said solvent containing from thirty-six to two hundred and fifty parts by volume of a refined petroleum hydrocarbon solvent having a specific gravity of about .70 to .85 and approximately fifteen parts by volume of a solvent from the group consisting of pine oil and terpinyl ethylene glycol monoether, said water being in an amount from eight to one hundred and fifty times the volume of all other ingredients, and said emulsion containing as an emulsifying agent triethanolamine oleate.

4. A liquid cleaning material for use when mixed with water, comprising a homogeneous nonaqueous mixture of a grease solvent the major portion of which is refined petroleum hydrocarbon solvent having a specific gravity of about .70 to .85, and a water soluble emulsifying agent in an amount insufficient to emulsify all of said grease solvent when the mixture is combined with water in an amount from eight to one hundred and fifty times the volume of the cleaning material, said emulsifying agent being present in the amount of at least one part to each 40 parts of said grease solvent by volume.

5. A liquid corrosion inhibiting and cleaning material for use when mixed with water, comprising a homogeneous nonaqueous mixture of a grease solvent the major portion of which is refined petroleum hydrocarbon solvent having a specific gravity of about .70 to .85, and a water soluble oleate soap in an amount insufficient to emulsify all of said grease solvent when the mixture is combined with water in an amount from eight to one hundred and fifty the volume of the cleaning material, said soap being present in the amount of at least one part to each 40 parts of said grease solvent by volume.

6. A liquid corrosion inhibiting and cleaning material for use when mixed with water, comprising a homogeneous nonaqueous mixture of a grease solvent the major portion of which is refined petroleum hydrocarbon solvent having a specific gravity of about .70 to .85, and a water soluble ethanolamine oleate in an amount insufficient to emulsify all of said grease solvent when the mixture is combined with water in an amount from eight to one hundred and fifty times the volume of the cleaning material, said oleate being present in the amount of at least one part to each 40 parts of said grease solvent by volume.

7. A corrosion inhibiting and cleaning material for use on metal when mixed with water, comprising a homogeneous mixture of from thirty-six to two hundred and fifty parts by volume of a petroleum hydrocarbon grease solvent having a specific gravity of about .70 to .85, approximately fifteen parts by volume of a material from the group consisting of pine oil and terpinyl ethylene glycol monoether, and a water soluble oleate soap, said soap being present in an amount insufficient to emulsify all of the solvent when the material is mixed with water in an amount in excess of eight times the volume of the cleaning material, said soap being present in the amount of at least one part to each 40 parts of the total solvent by volume.

8. A corrosion inhibiting and cleaning material for use on metal when mixed with water comprising a homogeneous nonaqueous mixture of from thirty-six to two hundred and fifty parts by volume of a petroleum hydrocarbon grease solvent having a specific gravity of about .70 to .85, approximately fifteen parts by volume of a material from the group consisting of pine oil and terpinyl ethylene glycol monoether, and triethanolamine oleate, said oleate being present in an amount insufficient to emulsify all of the solvent when the material is mixed with water in an amount in excess of eight times the volume of the cleaning material, said oleate being present in the amount of at least one part to each 40 parts of the total solvent by volume.

9. A liquid cleaning material for use when mixed with water, comprising a homogeneous nonaqueous mixture of a grease solvent the major portion of which is refined petroleum hydrocarbon solvent having a specific gravity of about .70 to .35, a water soluble emulsifying agent in an amount insufficient to emulsify all of said grease solvent when the mixture is combined with water in an amount from eight to one hundred and fifty times the volume of the cleaning material, and a blending agent in an amount sufficient to blend said material into a homogeneous mixture, said emulsifying agent being present in the amount of at least one part to each 40 parts of said grease solvent by volume.

10. A liquid corrosion inhibiting and cleaning material for use when mixed with water, comprising a homogeneous nonaqueous mixture of a grease solvent the major portion of which is refined petroleum hydrocarbon solvent having a

specific gravity of about .70 to .85. a water soluble oleate soap in an amount insufficient to emulsify all of said grease solvent when the mixture is combined with water in an amount from eight to one hundred and fifty times the volume of the cleaning waterial, and a blending agent in an amount sufficient to blend said material into a homogenous mixture, said soap being present in the amount of at least one part to each 40 parts of said grease solvent by volume.

11. A liquid corrosion inhibiting and cleaning material for use when mixed with water, comprising a homogeneous nonaqueous mixture of a grease solvent the major portion of which is refined petroleum hydrocarbon solvent having a specific gravity of about .70 to .85, a water soluble ethanolamine oleate in an amount insufficient to emulsify all of said grease solvent when the mixture is combined with water in an amount from eight to one hundred and fifty times the volume of the cleaning material, and a blending agent in an amount sufficient to blend said material into a homogeneous mixture, said oleate being present in the amount of at least one part to each 40 parts of said grease solvent by volume.

12. A corrosion inhibiting and cleaning material for use on metal when mixed with water, comprising a homogeneous mixture of from thirty-six to two hundred and fifty parts by volume of a petroleum hydrocarbon grease solvent having a specific gravity of about .70 to .85, approximately fifteen parts by volume of a material from the group consisting of pine oil and terpinyl ethylene glycol monoether, approximately one to two parts ethylene glycol monobutyl ether, and a water soluble oleate soap, said soap being present in an amount insufficient to emulsify all of the solvent when the material is mixed with water in an amount in excess of eight times the volume of the cleaning material, said soap being present in the amount of at least one part to each 40 parts of the total solvent by volume.

13. A corrosion inhibiting and cleaning material for use on metal when mixed with water, comprising a homogeneous nonaqueous mixture of from thirty-six to two hundred and fifty parts by volume of a petroleum hydrocarbon grease solvent having a specific gravity of about .70 to .85, approximately fifteen parts by volume of a material from the group consisting of pine oil and terpinyl ethylene glycol monoether, approximately one to two parts ethylene glycol monobutyl ether, and triethanolamine oleate, said oleate being present in an amount insufficient to emulsify all of the solvent when the material is mixed with water in an amount in excess of eight times the volume of the cleaning material, said oleate being present in the amount of at least one part to each 40 parts of the total solvent by volume.

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