METHOD FOR REMOVING OIL LUBRICANT FILM FROM STEEL

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This application is a continuation-in-part of application Serial No. 727,280, filed April 9, 1958, now abandoned.

This invention relates to the removal of lubricant film from metals, and more particularly to the application of a specific type of water mixture, or emulsion, in the removal of such film.

In the cold working of metals, wherein lubricants are used under extreme pressure, as in the cold rolling of strip, a rather tightly adherent film tends to build up on the metal surface. This film may result in objectionable metal surface conditions when the cold worked metal is given a subsequent finishing treatment.

When steel strip is subjected to cold reducing, a lubricant, often palm oil or a palm oil substitute, is applied to the strip before the strip enters the rolling mill. Generally, four-or-five-stand tandem mills are used in the cold reducing operation, and fresh lubricant may be applied before each roll stand. Because of the extreme heat generated in the rolling operation, the lubricant is usually added as an oil in water emulsion, the water having the function of heat dissipation. In spite of the cooling effect of the water, the strip temperature, on certain mills, becomes such that there is often considerable breakdown of various lubricants as the strip passes through the rolls. When the oil breaks down, a rather tenacious film develops on the strip. This film usually contains oil fragments, iron soaps, varnish-like condensation products and some original oil.

When this lubricant film is not removed, or is only partially removed from the strip, serious surface defects may develop during the annealing step which follows cold rolling. Common defects, which show up on the strip after it is removed from the annealing furnace, are carbonaceous deposits, which appear as smudge or "dirt" over the surface of the strip, staining and carbon edge. Carbon edge occurs as a hard coating actually extending into the metal surface, and it is commonly found near the edge of strip which has been box-annulled in coils. This form of defect can only be removed by abrasives or by buffing, and portions of strip containing carbon edge cannot be used as prime stock. The so-called "dirt," in the form of a carbonaceous deposit, can be removed from the strip by a rubbing action, but its removal adds a costly and time-consuming operation to the production of finished strip.

To insure against rejects, due to the various defects described above, a minimum of lubricant film should be present on the strip during annealing. In practice the film is effectively removed by a separate washing procedure, which involves unwinding the coil and passing the strip through a hot, strongly alkaline bath, followed by rinsing, drying and recoiling. The strip is then clean and ready for annealing. To avoid this extra procedure, it is often common in the industry to omit the application of oil at some point near the end of the tandem mill and to substitute at this point a dinitro solvent emulsion, or a detergent solution. By this means, the amount of oil film left on the rolled metal may be reduced to such an extent that the strip will be relatively clean and can be annealed directly after rolling, without any intervening cleaning step. However, some rolling oils, notably palm oil and tallow based oils, often break down, as noted above, to produce a film stubbornly resistant to all commonly used detergents or solvent emulsions. Detergents or cleaners, which may be effective in the removal of new palm oil, or new tallow-based oils, are often little more effective than water for the removal of the break-down products of such oils. Cleaners composed of loosely emulsified petroleum spirits, or oils, are only partially effective against such break-down oil films.

An object of this invention is to provide a composition and method for the satisfactory removal of lubricant film from cold-worked metal.

According to the present invention, the lubricant film, which remains on a metal surface after a cold-working operation, can be removed by the application of a water mixture, or emulsion, of certain insoluble fatty alcohols and alcohol derivatives of monoterpenes. The monoterpenes may be acyclic or cyclic. I have found that when a water emulsion of the foregoing alcohols or alcohol derivatives is applied to the surface of steel strip which has an adherent film composed largely of break-down products of a lubricant, that the film is substantially completely removed from the metal surface.

Alcohols which are particularly effective for use in this invention are those water-insoluble fatty alcohols having from 6 to 18 carbon atoms, including such compounds as hexyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, cetyl, stearyl and oleyl alcohols, and their isomers. Compounds representative of the alcohol derivatives of terpenes are e-terpineol and geraniol. These materials have superior solvent action on lubricant film break-down products.

An example of a satisfactory treating mixture, composed of an emulsion of an alcohol, is that which contains water and decyl alcohol wherein the weight ratio of water to said alcohol ranges from 5:1 to 5:1.

The emulsion of water and alcohol cleaner may be made by merely mixing the two with rapid stirring. A more practical type of emulsion, however, one which will retain its emulsion characteristics over a sufficient interval of time, can be prepared by the incorporation of an emulsifying agent. When about 5% emulsifying agent, based on the weight of alcohol in the mixture, is used, a temporary emulsion is formed. Emulsifying agent in the amount of 10% will produce a more permanent type of emulsion. The temporary form of emulsion is the most efficient in most circumstances, for in this unstable form substantially all of the alcohol is released in a reactive condition, when the emulsion comes in contact with the film-coated metal.

The present invention has proved quite effective in the treatment of cold-rolled strip, the effectiveness being illustrated by the following examples:

Example 1

A mill test was run using an emulsion formed by a mixture of the following ingredients:

<table>
<thead>
<tr>
<th>Parts</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>100</td>
</tr>
<tr>
<td>Iso-decyl alcohol</td>
<td>1.0</td>
</tr>
<tr>
<td>Emulsifier</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The emulsifier was a blend of three volumes of Igepal CO-530 and one volume of Igepal CO-630, both being non-ionic, alkyl phenoxypolyoxyethylene ethanol surfactants.

The emulsion was tested on a four-stand, high speed tandem mill for the cold reduction of 48 inch wide steel strip from 0.080 in. gage to 0.029 in. gage at a speed above 2000 ft. per minute. Reclaimed palm oil was used as the lubricant on the strip for the first stand of rolls, while "Palmoshield 1B," a proprietary triglyceride substitute for palm oil was used as lubricant for each of the two succeeding stands. The iso-decyl alcohol emulsion
cleaner was applied to the steel strip prior to the last stand of rolls and, in this particular case, also to the upper back-up rolls of stands three and four. The steel strip emerged from the mill with no residual oil film, and came out of the box annealing operation very clean and entirely free of so-called “dirt” and carbon edge. Previous coils run in the same work turn, using a commercial cleaner, had a greasy film and annealed dirty.

Example II

A mill test similar to that of Example I was made, wherein the emulsion contained 1.0 part of tridecyl alcohol in place of the iso-decyl alcohol of Example I. Two separate runs were made, with the emulsion having, in the first case, 50 parts of water, and in the second case, 100 parts of water. Using the emulsion containing 50 parts of water, steel strip was reduced from 0.0060 in. gage to 0.015 in. gage, the emulsion being sprayed on the strip prior to the fourth stand. The rolling was quite satisfactory and produced film-free coils that annealed clean. Similarly, using an emulsion containing 100 parts of water for dilution, steel was reduced to 0.017 inch gage. The strip from this latter test also annealed clean with no carbon edge or so-called “dirt.” In all cases, “dirt” was evaluated after annealing by a standard technique of holding a white paper towel against the rapidly moving steel strip as it was unwound and fed to the skin-pass (surface finishing) mill.

While in the examples, single alcohols have been used in the emulsion as the cleaning medium, the invention is not restricted to such use. Mixtures of alcohols, of the class specified, may be used as the cleaner.

It should be pointed out that the amounts of water and alcohol, used in the cleaner mixture, need not be limited to those given in the several examples. The amount of water used may range from approximately 50 parts to as much as 200 parts, while the alcohol content may vary from 0.4 part to 10 parts, or, in other words, a 500:1 ratio of water to alcohol at the one extreme, to a ratio of 5:1 of water to alcohol at the other extreme. The ratios just given are weight ratios. While the composition in Example I was actually made on a volume basis, there is no significant difference in the ratios, as a practical matter, whether given by weight or by volume. For example, in the composition of Example I, 1.0 part by volume of iso-decyl alcohol would represent 0.835 part by weight. The specific amounts of water and alcohol, to be used for any given cleaning operation, will depend on the nature of the material to be treated, i.e., the type of metallic surface and the type of lubricant used, as well as on the operating conditions, for example, the speed of travel in the case of rolled strip.

Certain organic solvents, for example kerosene or mineral spirits, may be mixed with the alcohol-water emulsion. The addition of an organic solvent is effective in certain cases in increasing the fluidity of the detergent, while at the same time having no adverse effect on the detergent properties of the alcohol.

Another mill test, similar to those of Examples I and II, was run using a mixture of alcohols and a reduced quantity of emulsifier as follows:

Example III

| Water       | 75 |
| Iso-decyl alcohol | 0.5 |
| Tridecyl alcohol | 0.5 |
| Emulsifier | 0.0033 |

The emulsifier was Igepal CO-630. The emulsion was used on the same four stand tandem mill as were Examples I and II, but for rolling heavy gage of between 0.060 in. to 0.030 in. Much of the strip in this test was 48 inches in width. The test was run under actual production conditions, and covered a span of three turns, or 24 hours. In rolling heavy gage material it is the practice to remove more of the rolling oil, and for this reason sprays of the cleaner mixture were directed onto both the top and bottom sides of the strip prior to stands three and four, and on the upper backup roll of number four stand. The strip was quite dry and free from oil as it came from the mill. The strip came out of the subsequent box annealing very clean without the use of any intermediate cleaning operation.

Satisfactory temporary emulsions can be made with the higher alcohols by using surfactants, or emulsifiers, other than those shown in Examples I, II and III. Other compositions have been tested in a laboratory apparatus designed to compare the cleaning compositions on soiled or coated test panels. The apparatus has been used extensively to screen various cleaning compositions prior to utilizing them in actual mill testing. The results of the laboratory tests have been found to correlate well with actual mill results.

The test procedure consisted in allowing a heated quan:

ity of dispersion to drop onto a steel panel which has been coated with used rolling oil containing iron soaps and polymers.

The apparatus consisted of a 250 ml. capacity glass separator funnel wrapped with electrical heating tape to maintain a temperature of 100° C. in the test solutions, or dispersion. A spiral blade stirrer was used to keep the test material dispersed.

A standard volume of 100 ml. of test dispersion was heated to 100° C. and put into the heated separator funnel while stirring was maintained therein. The stop-cock was opened full and dispersion allowed to run out, it dropping a distance of exactly 24 inches onto a 3 in. by 6 in. steel test panel inclined at an angle of 45°.

The point of impingement was one inch from the upper end of the panel. The area of a panel subject to cleaning by impingement, outward flow and run-off, the total surface area of the test solution amounted to from 13 to 15 square inches. A cleaned area of 13 square inches was considered excellent.

The test panels were thinly coated with a mixture consisting of 8% lamp black and 92% of recovered, used tallow-

based rolling oil containing the varnish-like degradation products formed by the heat and pressure of the mill. Lamp black was added merely for the purpose of rendering the coating readily visible. The degradation products included iron soaps and polymers formed from the oil. Such oil for this test was obtained from the used oil sludge in the oil sewer beneath the tandem mill. The sludge was dried and the oil extracted with diethyl ether. The filtered and dried ether extract was much more tacky than the new oil, and extremely more re-

sistant to its removal by proprietary cleaners and sur-

factants. The proprietary cleaners and all the common surfactants tested were able to clean only a small area at the point of immediate impingement of the stream on the panel. In most cases the result was a partial cleaning of from 34 to 3 square inches. This used oil was considered more characteristic of that encountered in actual practice on the tandem mill. The oil was consequently used for coating the test panels rather than new undamaged oil which presents no particular removal problem.

As a control for the laboratory test examples, the composition given in Example I (mill test) was tried in the apparatus at a dilution of 75 to 1. This resulted in a cleaned area of 13 square inches.

The previous examples (representing mill tests) used nonyl phenoxypolyethylenes ethoxylates compounds to cause the higher alcohols to form temporary emulsions capable of lasting up to the point of application at the strip surface. Other surface active compounds may be used to accomplish the same result without materially impairing the ability of these alcohols to clean metal surfaces. The following three examples successfully employed a different non-ionic surfactant, an anionic surfactant respectively to form a suitable temporary emulsion with the higher alcohol.
Example IV

Iso-decyl alcohol was mixed with 1% by weight of Tween 85 (Atlas Chemical Industries), a poloxylene from sorbitan trioleate. One volume of this mixture was then diluted with 75 volumes of water. A 100 ml. portion of the aqueous mixture was heated to 100°C, and then dropped onto a coated panel as previously described. All of the contents of the panel which was exposed to the stream and to its run-off was effectively cleaned to the extent of about 14 square inches.

Example V

Iso-decyl alcohol was mixed with 1% by weight of Santomerse D (Monsanto Chemical Company), an alkyl benzene sodium sulfonate, anionic surfactant. One volume of this mixture was diluted with 75 volumes of water and the resultant mixture tested on a coated panel as in Example IV. The resulting cleaned area was measured to be about 12.5 square inches.

Example VI

Iso-decyl alcohol was mixed with 5% by weight of Hyamine 1622 (Rohm & Haas Company), para diisobutyl phenoxy ethyl dimethyl benzyl ammonium chloride monohydrate, a non-ionic surfactant. One volume of this mixture was diluted with 75 volumes of water and tested as in Examples IV and V. The cleaned area amounted to about 13 square inches.

While my invention has been described as a method for the treatment of the surfaces of ordinary steel, it is also applicable in the cleaning of surfaces of stainless steel. The emulsion treatment is not confined to flat or rolled surfaces, but may also be used in the removal of lubricant film from wire and other extruded metal articles. Another quite useful application is in the washing of cold-rolled steel strip prior to electroplating, in which use the cleaning emulsion eliminates the necessity of an alkaline cleaner.

I claim:
1. The method of removing an oily lubricant film containing iron soaps from a steel surface coated with said film which comprises applying to said coated surface an aqueous mixture consisting essentially of water and from 0.20% to 20.0% by weight of a member of the group consisting of α-terpineol, geraniol, mixtures of α-terpineol and geraniol, water-insoluble fatty alcohols having from 6 to 18 carbon atoms and mixtures of said fatty alcohols having from 6 to 18 carbon atoms.
2. The method of removing an oily lubricant film containing iron soaps from a steel surface coated with said film which comprises applying to said coated surface an aqueous mixture consisting essentially of water and α-terpineol, geraniol, mixtures of α-terpineol and geraniol, water-insoluble fatty alcohols having from 6 to 18 carbon atoms and mixtures of said fatty alcohols having from 6 to 18 carbon atoms.
3. The method of removing an oily lubricant film containing iron soaps from a steel surface coated with said film which comprises applying to said coated surface a non-stable emulsion of said water and said ionic emulsifier to produce a non-stable emulsion with said water and said member ranges.
4. The method of removing an oily lubricant film containing iron soaps from a steel surface coated with said film which comprises applying to said coated surface an aqueous mixture consisting essentially of water and a member of the group consisting of α-terpineol, geraniol, mixtures of α-terpineol and geraniol, water-insoluble fatty alcohols having from 6 to 18 carbon atoms and mixtures of said fatty alcohols wherein the weight ratio of water to said member ranges from 500:1 to 5:1.
5. The method of removing an oily lubricant film containing iron soaps from a steel surface coated with said

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