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METAL COATING MIXTURE

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This invention relates generally to a special compound or mixture particularly adapted for preventing the rusting of bright steel surfaces, particularly such as those obtained by pickling, or by pickling and cold rolling, or by annealing in a controlled atmosphere, which steel is to be subsequently subjected to various cold forming operations such as spinning, cold rolling, stamping, drawing, and pressing. However, the compound or mixture may have other uses.

In the case of all steel articles, it is desirable to perform certain operations at the steel making plant. These operations include the pickling, generally the cold rolling, and sometimes part of the forming. These partly processed articles are then bundled and shipped to fabricating shops where the other operations necessary to produce the finished product are performed. Almost without exception these last operations require a bright surface practically free from rust. Without some protective coating these articles are prone to rust or corrode very rapidly, and frequently the corrosion that occurs in transit renders the material unsuitable for the finishing operations without repickling, which in many cases cannot be done.

This rusting cannot always be prevented by protecting the material by placing it in packages, or even by enclosing it in water-proof containers, because the steel is subjected in transit to different atmospheric conditions which cause the material to "sweat." For example, as the steel cools down during a cold night and is subsequently transferred to a warmer and more humid atmosphere, some moisture in the air condenses on the steel surface.

This rusting can be, of course, prevented by application of a varnish, but ordinary varnish, paint, etc. cannot be used because they interfere with the forming operations and cannot be readily removed. It has been found that for some purposes a satisfactory coating which will permit the subsequent forming operations is a petroleum oil described as a fraction that is lighter, i. e., having lower boiling, flash, and fire points, and having a lower viscosity than the oils generally used for lubricating purposes. The application of such oils, however, gives only temporary protection, often for a very brief period of but 2 or 3 days, when the material is subjected to varying atmospheric conditions. The cause for the failure of these oils to afford adequate protection is explained as follows:

From experiments the present inventor has ascertained that water in the vapor phase, as it exists in the air to produce humidity, is capable of penetrating a film of petroleum oil. Therefore, when articles made of steel with a bright surface and coated only with a petroleum oil, are exposed to a low temperature and then to a warmer, more humid atmosphere, the water vapor penetrates the oil film and condenses on the surface of the steel beneath the film. Since this vapor is saturated with oxygen, rusting of the steel surface beneath the oil progresses rapidly. Furthermore, he has observed that petroleum oil absorbs the oxygen of the air and, where the oil is in contact with an element for which oxygen has a high affinity, such as a moist steel surface, the oil continuously transfers the absorbed oxygen to this surface. Therefore, the rapid rusting of the surface continues indefinitely due to the fact that the oil film, while continuously feeding oxygen to the surface of the steel, tends to prevent the evaporation of the water beneath the film of oil even though the steel itself becomes warmer.

Other factors in part responsible for the above phenomenon are the relative densities of water and of the petroleum oils, and of their molecular attractive forces of adhesion, cohesion, and surface tension. The densities of all the petroleum oils are less than the density of water, so that once water in the liquid phase forms beneath the oil, the latter rises to the surface of the former. This lifting of the oil film by the water is made easier by the fact that the adhesive forces of the oil for the steel are no greater, or are less, than the adhesive forces of water for the steel, and the cohesive forces of both the oil and the water are greater than their adherence for each other. Furthermore, the interfacial tension of the oil film at the surface of the steel is high, causing the film to withdraw or retract to form progressively heavier films, ultimately collecting in pools on horizontal surfaces, or causing the film to creep from slightly inclined surfaces, these leaving no film or a discontinuous film on the surfaces sought to be protected.

The requirements of a coating suitable for the purposes embraced by the present invention are as follows:

1. The mixture should be practically odorless.
2. It must give off practically no vapors at atmospheric temperatures.
3. It must not be inflammable at temperatures below 300 degrees Fahrenheit, and should have a fire point not lower than 350 degrees Fahrenheit, and burn but slowly, or not at all, to eliminate fire hazards.

4. The material must not contain any toxic substance, so that any vapors (smoke or fume) given off at elevated temperatures, are without physiological effect upon the workmen and are otherwise practically harmless.

5. The various ingredients should form a homogeneous liquid mixture, from which any rust inhibitors used do not separate on standing or with change of temperature, thus insuring uniformity of the coating under the same operating conditions, and avoiding the mottled appearance of some coatings and the speckled surface obtained when the coating contains particles in suspension.

6. Its flowing and adhesive properties should be such that dipping gives a coat uniformly distributed over the surface of the steel, the excess draining off rapidly but leaving a film that will not drain off entirely from a vertical surface.

7. The coating should be soluble in kerosene, gasoline, light lubricating oils and other solvents, so that it can be cheaply removed if necessary.

8. The coating should be practically non-oxidizing and non-hardening so that it can, if desired, be wiped off with a cloth after standing several months.

9. Some of the coating should remain on the steel surface after heating to 600 degrees Fahrenheit, and the part remaining at this temperature should retain its characteristic properties and should not char.

10. The base oils should give a very low carbon residue, so that trouble from "chars" formed by heating is avoided.

11. The coating should preferably have a light color, and form a translucent film, and it must not contain inorganic pigments or mineral matter of any kind which would injure the tools or prevent a smooth surface finish on the article being formed.

12. The color and capacity of the film should be such that it will not mask the appearance of rust on the steel surface beneath it.

13. The coating must not cause the pieces in contact in a bundle to stick together, that is, to adhere closely to each other.

14. The coating should be capable of protecting the steel from rusting for periods of 6 months or longer under the varying atmospheric conditions of transportation and storage under cover.

15. The components of the mixture must all be free of substances corrosive to steel, such as acidic compounds, oxidizable sulphur compounds, etc.

16. The coating mixture must be very cheap and adaptable to any of the methods in use for applying coatings to steel surfaces, such as dipping, spraying, brushing, passing through rolls covered with fabrics saturated with the mixture, etc.

It is evident that many petroleum oils meet some of these requirements, but for reasons given above, they fail in the most essential one, namely, the prevention of corrosion and rusting. However, it is desirable to use these oils as a base for cheap coatings, and the present inventor has directed his researches to discover substances that could be mixed with them to prevent the penetration of their films by water in the vapor phase, to improve their adhesive properties for steel surfaces, and to overcome the tendency of these oils to absorb oxygen from the air. As is well known, these oils are composed mainly of the heavier paraffins, which are carbon-hydrogen compounds of the chain series having the general formula $C_nH_{2n}+2$.

The present inventor has found that the residue from turpentine, which is a complex mixture of resins dissolved in terpenes, principally dextro and laevo-pinene, also designated as alpha pinene and beta pinene, forms an effective coating to protect from rusting, particularly if a slight film of oxide is already formed on the surface. The terpenes are cyclic hydrocarbons; the pinenes having the formula $C_{10}H_{16}$.

In the use of turpentine these pinenes evaporate, leaving the residue. Since the terpenes make up most of the turpentine and the latter product is costly, the protective coating obtained by the use of turpentine alone is expensive because of the large volume of turpentine required to obtain a sufficient amount of residue on the surface. Turpentine mixed with petroleum oil produces a mixture that is ineffective as an agent for preventing corrosion unless it is mixed with an oxygen-absorbing agent which has a greater chemical affinity for oxygen than iron has.

Others had already found that "refuse palm oil," a waste product from the tinning of steel sheets, affords a protection against atmospheric corrosion when applied after being thinned with kerosene or other light petroleum products. This inventor's examination of this waste product indicated that it is made up partly of a tarry decomposition product of palm oil and that it has: (1) high adhesive forces for steel surfaces, (2) strong attractive forces between it and the surface film of water, (3) surface tension effects that are the direct opposite of the petroleum oil, and (4) properties similar to turpentine residues obtained by open distillation of the terpenes.

This "refuse palm oil" is produced from palm oil in the tinning of steel sheets. In this process, palm oil is used on the top of the tin bath where it is subjected constantly to a temperature above 450 degrees Fahrenheit and exposed to the air and to the action of iron and tin compounds. Under these conditions, the palm oil undergoes slow changes, forming tarry-like constituents, until finally it is no longer usable in the tinning process. Palm oil is made up mainly of palmitic and oleic acids having the formula $C_{16}H_{32}O_2$ and $C_{18}H_{34}O_2$, respectively, and the glycerides of these acids. Both acids are chain series compounds, palmitic acid having the general formula $C_nH_{2n}O_2$ and oleic acid the general formula $C_nH_{2n-2}O_2$.

In the cold this product of the palm oil is almost a solid and does not mix readily with kerosene and the heavier petroleum oils. Nevertheless, this inventor has verified the findings of prior investigators, namely, that when it is mixed with such products the mixture is effective in preventing the rusting of bright steel surfaces. By experiment this inventor has found that turpentine dissolves the partly decomposed palm oil product, and if the tarry waste palm oil is heated until it melts or, in other words, to temperatures between 45 degrees and 50 degrees centigrade, the addition of a small proportion of turpentine causes the mixture to remain fluid at ordinary temperatures, and this mixture, when added to certain types of petroleum oils, not only mixes readily with the oil, but forms a mixture approximating the properties of a solution, so that neither the palm oil nor the decomposition products of the palm oil separate from the oil on standing or with change of temperature. In addition to its action maintaining the mixture fluid, the turpentine performs two other functions, one

of which is to supply a volatile constituent in the mixture, giving an "out-passing" component in the vapor phase which tends to block the intake of oxygen and of water, that are also in the vapor phase. The third function resides in the turpentine residue of waxes and gums which tend to react with the oxygen absorbed after the volatile compounds have been expelled, thus preventing the oxygen from reaching the surface of the steel.

By adding to the melted tarry palm oil a small amount of caustic soda or caustic potash, some of the undecomposed palmitic and oleic acids are saponified and the soap thus formed remains in the mixture as a buffer to neutralize any small amount of acids that may be either in the turpentine or in the petroleum oil, and react with traces of acids and ferrous salts that may remain on the surface of the steel. The use of the caustic soda or caustic potash is not always necessary, and other inorganic rust inhibiting compounds, such as sodium phosphate, may also be incorporated into the mixture. Furthermore, the soap thus formed, when mixed with a proper proportion of clean soft or softened water and applied to bright steel surfaces at temperatures high enough to cause rapid evaporation of the water, will inhibit the corrosion of the articles for several weeks, provided the steel is not exposed to open weather conditions.

In a further modification, one may add to the mixture, an organic substance which has a high affinity for oxygen in order to prevent corrosion completely or further retard and inhibit corrosion. Such an organic substance might be, for example, benzyl aminophenol, para bi-hydroxybenzene or potassium tri-hydroxybenzene.

As one example of the use of the oil preparation described above and of a suitable method of preventing corrosion, this inventor now gives in detail the treatment of an article that is to be pickled and partly fabricated at the steel works before shipment to the factory where it is further processed to give a finished product, this article being made from a thin steel plate.

The hot rolled plates are placed upon a rack and immersed in a pickling bath in the usual manner. The plates are permitted to remain in the acid solution until all scale has been removed; they are then washed in water kept neutral or slightly alkaline with milk of lime, and then, preferably, given another dip or wash in a similar slightly alkaline bath kept at a temperature above 100 degrees Fahrenheit. On being removed from this bath, the plates are allowed to drain dry, their temperature being such as to hasten the drying process. During the time the plates are thus exposed to the air a slight film of yellow to brown oxide may form on the surface, but usually this film is harmless and it is more desirable to permit it to form than to dip the plates into the oil mixture too soon, that is, before they are completely dried on all parts of all surfaces of each. While still warm and before they have cooled below the desired temperature for coating, they are dipped into the tank containing a suitable mixture made up of petroleum oil and the turpentine-tarry palm oil mixture which has been added in varying proportions to meet different conditions, these proportions being within the limits as set forth in the following paragraph. The plates are then removed from the bath and a portion of the oil mixture is allowed to drain from them. Then such fabricating operations as may be necessary are performed which may include shearing, punching, etc. After inspecting and bundling, the sheared edges are coated with the same mixture applied with a brush or otherwise.

The proportion in which the three ingredients making up the special rust-preventing oil mixture are mixed may be varied considerably to meet different conditions resulting from different seasons of the year and different ways of shipping materials of this kind. The range in proportions to meet all the conditions usually encountered, stated in parts by volume required to prepare approximately 100 gallons of the coating, is as follows:

Petroleum oil	Turpentine	Refuse palm oil
96	1	3
94	1	5
88	2	10
82	3	15
73	7	20

The proportions of the turpentine-"refuse palm oil" mixture are decreased when the atmospheric conditions are not severe, as in summer, for example, and the material is not to be long in transit or held for a long time exposed to such conditions. The proportions are increased with the time protection as desired, and to withstand severe atmospheric changes in temperature and humidity which may cause condensation of water on the surface of the steel. Increasing the proportions of the turpentine-"refuse palm oil" mixture will also increase the thickness of the coating for any given set of conditions. The petroleum oil must be supplied to certain specifications with respect to its fire point, its viscosity, and its pour-point temperature, these factors being varied within limits presecribed by safety laws, rules and regulations, and within these limits according to the thickness of coating desired.

The temperature at which the plates or other articles are dipped will also control the thickness of the coating. For example, with any given oil mixture, dipping the articles cooled to atmospheric temperatures will give the heaviest, that is, the thickest coating that will remain on the surface under these conditions, while articles dipped at higher temperatures will give correspondingly lighter coatings. To prevent corrosion of the surface, it is an object to apply the thickest coating that will remain upon the surface permanently and not give a large excess that will drain off and thus be wasted.

While it is possible to employ a very light petroleum oil such as kerosene, for general industrial use, safety and freedom from the fire hazard and the danger of explosion, an oil is required having a flash point at 250 degrees Fahrenheit or higher and a fire point at 300 degrees Fahrenheit or higher by the open cup method. Also, to permit ready handling under all weather conditions in a temperate zone of latitude, the oil should have a "pour-point", that is, a congealing temperature, not above —30 degrees Fahrenheit.

The present inventor has found that for the protection of some steel surfaces only a very thin film is required. Therefore, when it is possible to apply a thin film and equipment is available to make it possible to apply this mixture as an extremely thin even coating or to recover the turpentine that would otherwise evaporate into the air, the inclusion of petroleum oil as a low

priced diluent or vehicle for the refuse palm oil may be dispensed with and a mixture comprising turpentine and refuse palm oil only, may be used to give entirely satisfactory protection. In view of the oxygen-absorbing characteristics of petroleum oil, as mentioned above, these thin coatings may afford protection equal to the heavier coatings made with the mixture containing petroleum oil.

This inventor has found that oils made to the same specifications as determined by the ordinary standard methods with respect to flash point, fire point, viscosity, pour-point, specific gravity etc., may differ in three respects important for our purpose, namely, the ease or readiness with which they will dissolve or mix with the turpentine—"refuse palm oil" mixture, the tenacity with which they will adhere to a bright steel surface, and their spreading characteristics which determine the uniformity in the thickness of the adhering film. Simple trial tests are sufficient to permit anyone interested to select an oil best suited for the purpose.

It is understood that various modifications may be made in the methods for preparing the mixture and for applying it to the bright steel surfaces without departing from the scope of this invention, as defined by the following claims.

I claim:

1. A metal coating mixture comprising by volume 3 to 20 parts "refuse palm oil," from 1 to 7 parts turpentine and petroleum oil to make 100 parts, said petroleum oil having a flash point of at least 250 degrees Fahrenheit and a fire point of at least 300 degrees Fahrenheit as determined by the open cup method.

2. A metal coating mixture comprising by volume 3 to 20 parts "refuse palm oil," having an appreciable portion but not all of its undecomposed palmitic and oleic acids saponified, from 1 to 7 parts turpentine and petroleum oil to make 100 parts, said petroleum oil having a flash point of at least 250 degrees Fahrenheit and a fire point of at least 300 degrees Fahrenheit as determined by the open cup method.

3. A metal coating mixture comprising by volume 3 to 20 parts "refuse palm oil" and from 1 to 7 parts turpentine.

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