

[54] **METHOD OF IMPROVING
RESISTANCE TO CORROSION OF
METAL SURFACES AND RESULTANT
ARTICLE**

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132 R, 117/219, 224, DIG. 5; 252/388, 389, 33, 39

[56] **References Cited**

UNITED STATES PATENTS

3,084,066 4/1963 Dunmire 117/75
3,242,079 3/1966 McMillen 252/33

3,384,586 5/1968 McMillen 252/33
2,758,981 8/1956 Cooke et al. 252/39 X
2,834,691 5/1958 Stephenson et al. 117/75 X
3,372,114 3/1968 Rense 252/33

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[57] **ABSTRACT**

A method of improving resistance to corrosion of metal surfaces is disclosed, wherein said method comprises:

a. applying to the metal surface a composition comprising (1) a major amount (e.g. at least 75 weight percent) of a thixotropic, grease-like composition consisting essentially of a non-volatile diluent, an oil-soluble dispersing agent and an alkaline earth metal carbonate and (2) a minor amount (e.g. 0.1 to 25 weight percent) of a polymer, and

b. applying to the coated metal surface a conventional paint. An important feature is the use of the composition described in step (a) as a primer coating.

23 Claims, No Drawings

METHOD OF IMPROVING RESISTANCE TO CORROSION OF METAL SURFACES AND RESULTANT ARTICLE

RELATED APPLICATIONS

The following applications have the same assignee as the present application:

Ser. No. 727,719, filed May 8, 1968, now abandoned concerns a method of preparing the thixotropic, grease-like composition.

Ser. No. 729,875, filed May 8, 1968, now U.S. Pat. No. 3,565,672 concerns the use of a thixotropic, grease-like composition as a primer for paints.

The teachings of these applications will be discussed more completely hereinafter.

Ser. No. 20,039, filed the same day as the present application, concerns grease compositions comprising a major amount of a thixotropic, grease-like composition and a minor amount of a polymer.

BACKGROUND

The use of surface coatings (e.g. paint) to protect metals from corrosion is well-known. Usually, the corrosion protection is due more to the use of particular primers than to the paint itself. While most of the surface coatings (including primers) of the prior art afford a satisfactory degree of protection, they have the disadvantage that the surface requires a relatively high degree of preparation prior to the application of the primer. The high cost of the labor used in preparing the surface makes the total job of coating the metal surface quite expensive.

It is thus apparent that it would be highly desirable to have a primer which affords good corrosion protection and yet requires only a minimum amount of preparation of the metal surface prior to application. Application Ser. No. 729,875, referred to in the foregoing, teaches the use of a thixotropic, grease-like composition as a primer which meets these requirements. My invention provides a composition which gives improved results as a primer. Briefly stated, the composition of my invention comprises (1) a major amount of a thixotropic, grease-like composition and a minor amount (e.g. 0.1 to 25 weight percent) of a polymer having certain characteristics. The use of such a composition as a primer results in a film which is harder, tougher and less tacky than the use of the composition of application Ser. No. 729,875.

PRIOR ART

The most pertinent prior art is believed to be the following:

U.S. Pat. No. 3,384,586 teaches the addition of a thixotropic, grease-like composition to a polymer. More specifically, this patent teaches a composition comprising a major amount of a polymer and a minor amount of the thixotropic, grease-like composition.

U.S. Pat. No. 3,372,114 teaches that gelled materials useful as a lubricant additive in greases are prepared by contacting (A) a fluid mineral oil solution of a carbonated, basic complex of an alkaline earth metal and an organic carboxylic or sulfonic acid, salt thereof, or carboxylic ester containing at least 12 aliphatic carbon atoms, the complex being characterized by a metal ratio of at least 4:5, with (B) oxygen at a temperature of about 150° C. to about 300° C. The patent further teaches that in some instances the product is a grease and that small compatible hydrocarbon resins can be added to the product.

Neither of these patents contain any teachings that the compositions taught therein can be used as a primer for conventional paints.

Application Ser. No. 729,875 has been discussed in the section in the immediate foregoing.

BRIEF SUMMARY OF THE INVENTION

Briefly, the present invention concerns a method of improving resistance to corrosion of metal surfaces wherein the method comprises:

a. applying to the metal surface a composition comprising (1) a major amount (at least 75 weight percent) of a thixotropic, grease-like composition consisting essentially of a nonvolatile diluent, an oil-soluble dispersing agent and an alkaline earth metal carbonate and (2) a minor amount (0.1 to 25 weight percent) of a polymer, which, preferably, has the following properties:

i. a low degree of crystallinity,

ii. a molecular weight in the range of from about 3,000 to about 1 million, and

iii. a high solubility in predominantly aliphatic hydrocarbon solvents,

b. applying to the coated metal surface a conventional paint.

Preferably, the composition applied in step (a) should be substantially free of volatile solvents before applying the paint in step (b).

In another aspect, the present invention concerns a metal article having improved resistance to corrosion, said metal article having the exterior surface coated with the composition, described in the foregoing, as the primer coat and a conventional paint as the external coat.

In still another aspect, the present invention concerns the use of the composition, described in the foregoing, as a primer coating when used in conjunction with conventional paints on any of the surfaces normally coated by conventional paints.

DETAILED DESCRIPTION

The composition used in my invention comprises a major amount of a thixotropic, grease-like composition and a minor amount of a polymer having certain properties.

The thixotropic, grease-like composition consists essentially of the following materials in the amounts stated:

Parts by Weight

	Suitable	Preferred
Nonvolatile diluent*	2-80	20-70
Oil-soluble dispersing agent*	5-55	6-35
Alkaline earth metal carbonate*	1-45	5-30

*The specific nature of these materials will be described hereinafter in connection with the preparation of this composition.

The thixotropic, grease-like composition has the following properties:

An acetic base number of at least 50, preferably at least 135,

Dropping point, ASTM, of at least 480° F., Does not flow at 210° F. (*Another way of stating this property is that the composition has no apparent (i.e. cannot be measured) viscosity at 210° F.)

In order to described more fully the nature of the thixotropic, grease-like composition we will now describe methods of preparing the composition. In so doing we will describe the nature of the materials present in the composition.

Basically, there are two general methods of preparing the composition. The first method is called simply a "two-step" method. According to this method, a colloidal dispersion of alkaline earth metal carbonate is formed first. The dispersion is then treated, preferably, with a small amount of water in the presence of a small amount of alcohol. The second method is called simply a "one-step" method. According to this method, an admixture is formed of oil-soluble dispersing agent, nonvolatile diluent, alkaline earth metal compound, alcohol, and water. After treating the admixture with CO₂, the

volatile materials are removed by distillation. The two-step method will be described in detail first.

TWO-STEP METHOD OF PREPARATION

Starting Materials

The charge (or starting) material for this method of preparing the thixotropic, grease-like composition is a colloidal dispersion of an alkaline earth metal carbonate in a suitable diluent and having an acetic base number of at least 50. The term "alkaline earth metal" as used herein refers only to those of this group which are more commonly available, namely, magnesium, calcium, strontium and barium. Of these, calcium and barium are more suitable, with calcium being preferred.

While we have used the term alkaline earth metal carbonate it may be well to mention that, although carbonate is the predominant anion, traces of other anions, e.g. hydroxide, oxide, and alkoxide, can be present. This is due to the fact that many processes of preparing dispersions of alkaline earth metal carbonates prepare the carbonate by carbonation of an alkaline earth metal hydroxide, oxide or alkoxide.

Many processes are known for preparing colloidal dispersions of alkaline earth metal carbonates. Also, several processes are known for preparing colloidal dispersions of alkaline earth metal carbonates, wherein the metal carbonate is formed in situ in the presence of the dispersing agent. It is characteristic of the products prepared by the in situ method that they have a uniform and small (i.e. 0.25 micron or less, and usually 0.10 micron or less) particle size.

The following U.S. patents are concerned with the preparation of colloidal dispersions, wherein the alkaline earth metal compound is formed in situ: U.S. Pat. No. 3,150,089, to Mack W. Hunt, which issued Sept. 22, 1964 and is entitled "Highly Basic Magnesium-Containing Additive Agent"; U.S. Pat. No. 3,150,088, to Mack W. Hunt et al., which issued Sept. 22, 1964 and is entitled "Highly Basic Calcium-Containing Additive Agent"; U.S. Pat. No. 2,956,018 to Robert L. Carlyle et al., which issued Oct. 11, 1960 and is entitled "Metal Containing Organic Compositions and Method of Preparing the Same"; U.S. Pat. No. 2,937,991, to Robert L. Carlyle, which issued May 24, 1960 and is entitled "Method of Dispersing Calcium Carbonate in a Non-Volatile Carrier"; and U.S. Pat. No. 2,895,913, to Robert L. Carlyle et al., which issued on July 21, 1959 and is entitled "Magnesium Containing Organic Compositions and Method of Preparing the Same."

The colloidal dispersions which are used as a starting material consist essentially of a nonvolatile diluent, an oil-soluble dispersing agent, and an alkaline earth metal carbonate. These materials are present in the following range:

Parts by Weight

	Suitable	Preferred
Nonvolatile diluent	2-80	20-70
Dispersing agent	5-55	6-35
Alkaline earth metal carbonate	1-45	5-30

In addition to the nonvolatile diluent, oil-soluble dispersing agent, and basic metal compound, the colloidal dispersions may contain minor amounts of the alcohol which is employed in manufacturing the colloidal dispersion, and of the metal-containing intermediate which may be employed in manufacturing the colloidal dispersion.

A wide variety of nonvolatile diluents are suitable in the colloidal dispersions used as the starting material. The principal requisite desired in the nonvolatile diluent is that it will act as a solvent for the dispersing agent which is used. Examples of nonvolatile diluents which can be used include mineral lubricating oils obtained by any of the conventional refining procedures; liquid synthetic lubricating oils, vegetable oils,

such as corn oil, cotton seed oil, and castor oil; animal oils, such as lard oil and sperm oil; and waxes, such as the petroleum waxes. Of the waxes, the microcrystalline waxes are preferred. Of the oils in the preceding examples, the mineral lubricating oils are preferred.

It should be noted that when a wax is used as the nonvolatile diluent, the colloidal dispersion is a solid at room temperature.

A variety of oil-soluble dispersing agents are suitable in the colloidal dispersions which are used in preparing the product used in my invention. Generic examples of suitable dispersing agents include oil-soluble sulfonic acids, carboxylic acids, and the metal salts thereof. The preferred dispersing agents for preparing the grease-like product used in my invention, are the oil-soluble sulfonic acids and metal sulfonates.

The term "metal" as used in "metal sulfonates," refers to those metals which are conventionally used to prepare the metal sulfonates of commerce. This includes metal sulfonates wherein the metal is sodium, potassium, magnesium, calcium, and barium. The more suitable sulfonates are those wherein the metal is calcium or barium. Preferably, the metal of the metal sulfonate is the same as the metal of the basic metal compound.

The term "oil-soluble sulfonates," as used herein, refers to those sulfonates wherein the hydrocarbon portion of the molecule has a molecular weight in the range of about 300 to about 1,000. Preferably, this molecular weight is in the range of about 370 to about 700. These oil-soluble sulfonates can be either synthetic sulfonates or the so-called mahogany or natural sulfonates. The term "mahogany sulfonates" is believed to be well understood, since it is amply described in the literature. The term "synthetic sulfonates" refers to those sulfonates which are derived from sulfonation feedstocks which are prepared synthetically. The synthetic sulfonates include alkyl sulfonates and alkaryl sulfonates. The alkaryl radical can be derived from benzene, toluene, ethyl benzene, xylene isomers, or naphthalene. Preferably, the alkyl groups are branched chain.

Mixtures of sulfonates derived from alkaryl hydrocarbons having straight-chain alkyl groups and alkaryl hydrocarbons having branched-chain alkyl groups, and wherein the amount of sulfonate derived from branched-chain alkaryl hydrocarbons is at least 40 percent by weight, are particularly suitable. Preferably, the amount of sulfonate derived from branched chain alkaryls is at least 60 percent by weight.

An example of an oil-soluble alkaryl sulfonate (a synthetic sulfonate) which has been particularly useful in preparing colloidal dispersions is the material known as post-dodecylbenzene sulfonate. Postdodecylbenzene is a bottoms product of the manufacture of dodecylbenzene. The alkyl groups of postdodecylbenzene are branched chain. Postdodecylbenzene consists of monoalkylbenzenes and dialkylbenzenes in the approximate mole ratio of 2:3 and has typical properties as follows:

Specific gravity at 38° C.	0.8649
Average molecular weight	385
Percent sulfonatable	88
A.S.T.M. D-158 Engler:	
I.B.P., °F.	647
5 °F.	682
50 °F.	715
90 °F.	760
95 °F.	775
F.B.P. °F.	779
Refractive index at 23° C.	1.4900
Viscosity at:	
-10° C., centipoises	2800
20 centipoises	280
40 centipoises	78
80 centipoises	18
Aniline point, ° C.	69
Pour point, °F.	-25

An example of another oil-soluble synthetic alkaryl sulfonate, which is particularly useful for preparing colloidal dispersions, is the sulfonate derived from a sulfonation feed-

stock known as "dimer alkylate." "Dimer alkylate" has branched-chain alkyl groups as does postdodecylbenzene. Briefly described, dimer alkylate is prepared by the following steps:

1. Dimerization of a suitable feedstock, such as cat poly gasoline,
2. Alkylation of an aromatic hydrocarbon with the dimer formed in step (1).

Preferably, the dimerization step uses a Friedel-Crafts alkylation sludge as the catalyst. This process and the resulting product are described in U.S. Pat. No. 3,410,925.

An example of still another oil-soluble synthetic alkaryl sulfonate, which is particularly useful for preparing colloidal dispersions, is the sulfonate derived from a sulfonation feedstock which I refer to as "NAB Bottoms." NAB Bottoms are predominantly di-n-alkaryl, wherein the alkyl groups contain from eight to 18 carbon atoms. They distinguish primarily from the preceding sulfonation feedstocks in that they are straight-chain and contain a large amount of di-substituted material. The process of preparing these materials and the resulting product are described in application Ser. No. 521,794 filed Jan. 20, 1966, now abandoned, and having the same assignee as the present application. Another process of preparing a di-n-alkaryl product is described in application Ser. No. 529,284, filed Feb. 23, 1966, now abandoned and having the same assignee as the present application.

Mixtures of sulfonates derived from "dimer alkylate" and "NAB Bottoms" are suitable for preparing the grease-like compositions used in my invention.

In order to make my disclosure even more complete, U.S. Pat. No. 3,410,925 and application Ser. Nos. 521,794 and 529,284 are made a part of this disclosure.

Other sulfonates which can be used in the colloidal dispersion employed as a starting material include, for example, mono- and poly-wax substituted naphthalene sulfonates, dinonyl naphthalene sulfonates, diphenyl ether sulfonates, naphthalene disulfide sulfonates, diphenyl amine sulfonates, dicetyl thianthrene sulfonates, dilauryl betanaphthol sulfonates, dicapryl nitro-naphthalene sulfonates, unsaturated paraffin wax sulfonates, hydroxy substituted paraffin wax sulfonates, tetramylene sulfonates, mono- and poly-chloro-substituted paraffin wax sulfonates, nitrosoparaffin wax sulfonates; cyclo-aliphatic sulfonates, such as lauryl-cyclohexyl sulfonates, mono- and poly- wax substituted cyclohexyl sulfonates, and the like.

In addition, it is to be understood that the metal salts of the preceding sulfonates can be formed in situ during preparation of the colloidal dispersion by neutralization of the corresponding sulfonic acid.

Suitable carboxylic acids which can be used in preparing the colloidal dispersion used as a starting material include naphthenic acids, such as the substituted cyclopentane monocarboxylic acids, the substituted cyclohexane monocarboxylic acids and the substituted aliphatic polycyclic monocarboxylic acids containing at least 15 carbon atoms. Specific examples include cetyl cyclohexane carboxylic acids, dioctyl cyclopentane carboxylic acids, dilauryl decahydronaphthalene and stearyloctahydro indene carboxylic acids and the like and oil-soluble salts thereof. Suitable oil-soluble fatty acids are those containing at least eight carbon atoms. For producing the colloidal dispersion in liquid form, I prefer fatty acids which are liquids at ambient temperatures down to about 15° C. Specific examples include 2-ethyl hexanoic acid, pelargonic acid, oleic acid, palmitoleic acid, linoleic acid and ricinoleic acid. Naturally occurring mixtures of predominantly unsaturated fatty acids, such as tall oil fatty acids, are particularly suitable.

In addition, it is to be understood that the metal salts of the preceding carboxylic acids can be formed in situ during preparation of the colloidal dispersion by neutralization of the corresponding carboxylic acid.

Process Conditions (Two-step Method)

The thixotropic grease-like composition used to prepare the composition of my invention can be prepared by treating the colloidal dispersion with a small amount of water in the presence of a small amount of an alcohol. From a practical viewpoint, the amount of water which is used should be at least about 3 percent, preferably about 7 percent, by weight, based on the colloidal dispersion. Preferably, the amount of water should not be above 12 percent, and usually not above 20 percent, by weight, based on the colloidal dispersion. (Larger amounts can be used conceivably, but no advantage results therefrom. Also, if an extremely long reaction time can be tolerated, an amount of water less than 3 percent might be used.) It should be noted that I have found that increasing the amount of water from 4 or 5 percent to about 7 or 8 percent provides a pronounced increase in rate of reaction.

The amount of alcohol which is used is in the range of about 0.5 to about 10 percent, preferably from about 1 to about 5 percent, by weight, based on the colloidal dispersion. These aforementioned amounts of alcohol include the residual alcohol present in the colloidal dispersion which runs from about 0.5 percent to about 3 percent by weight, usually.

It is apparent from the preceding that some colloidal dispersions have sufficient residual alcohol so that additional alcohol is not required. Sometimes, the use of additional alcohol will accelerate the reaction rate. Also, the amount of alcohol required varies with the type of dispersing agent, in that some dispersing agents require more alcohol than others. Furthermore, the alcohol which is added does not have to be the same species of alcohol which is present as the residual alcohol.

A wide variety of alcohols can be used in the conversion of the colloidal dispersion to the thixotropic, grease-like composition used in my invention. Examples of suitable alcohols include the C₁-C₁₀ alkanols, the monoether alcohols of ethylene glycol containing up to eight carbon atoms, and the monoether alcohols of diethylene glycols containing up to eight carbon atoms. Preferably, the alcohols have boiling points of at least about that of water. Examples of suitable alcohols include methanol, ethanol, propanol, isobutanol, pentanol, hexanol, octanol, decanol, 2-methoxy ethanol, and 2-ethoxy ethanol. Of these isobutanol and 2-methoxy ethanol are preferred.

As is apparent from the preceding discussion, an important feature of the process of preparing the grease-like composition is the use of a combination of water and an alcohol to effect a modification reaction. By "modification reaction" is meant the change from a fluid, clear colloidal dispersion to a viscous, tacky material.

In the preparation of the composition, heat is applied to the admixture containing colloidal dispersion, water, alcohol (and, possibly, volatile solvent or nonvolatile diluent oil). The heat is applied until the modification reaction occurs which is apparent by a rapid change in viscosity of the reaction admixture. The modification reaction occurs at a temperature slightly above 170° F. Usually a temperature of 190°-210° F is sufficient to cause the reaction to go to completion rapidly.

In practicing the method of my invention it is often convenient to use a solution of the composition in a volatile solvent. When the composition is to be used thusly it is often convenient to prepare the thixotropic, grease-like composition in the presence of the volatile solvent. The polymer is then added to the solution. When the "modification reaction" is conducted in the presence of the volatile solvent, the occurrence of the reaction is still visible in that the viscosity changes and the solution changes from a bright, clear solution to a hazy or cloudy solution. The temperature employed and the total amount of heat used are not critical in the two-step method.

ONE-STEP METHOD OF PREPARATION

Starting Materials

The nature and amounts of the starting materials, which are used to prepare the thixotropic, grease-like composition which is used in the compositions of our invention, are shown in the following table:

Material	Parts by Weight	
	Suitable	Preferred
Nonvolatile Diluent	2-80	5-30
Dispersing Agent	2-65	5-35
Alkaline earth metal (Present as alkaline earth metal carbonate complex)	2-40	10-30
Water	1-6	2-4
Alcohol	10-40	20-30
Volatile Solvent (Optional*)	0-60	25-55

*Previously, in discussing the process conditions for the two-step method I stated that a volatile solvent, which often is used in applying the grease-like composition, can be present during the preparation. Preferably, however, in the two-step method the grease-like composition is prepared first and dissolved in the volatile solvent. In the one-step method there is no advantage in first preparing the grease-like composition and then dissolving it. In view of this having the volatile solvent present during the preparation of the composition is a matter of choice dependent on other factors. The nature of the volatile solvent is described hereinafter.)

It should be emphasized that the above-stated ranges apply solely to the one-step process of preparing the grease-like composition. The ranges differ from those given hereinafter for the grease-like composition per se, primarily, due to the inclusion of volatile materials. For this reason the ranges are stated solely to illustrate the process. Insofar as the above-stated ranges differ from those given for the grease-like composition per se my invention is limited only to the ranges stated for the composition.

Suitable and preferred nonvolatile diluent, dispersing agent and alkaline earth metal are the same as described previously in connection with the two-step method.

An alkaline earth metal carbonate, which is formed in situ, is used in the process. In forming the alkaline earth metal carbonate, an admixture is prepared of alkaline earth metal basic compound, selected from the group consisting of oxides, hydroxides, and alcoholates, dispersing agent, nonvolatile diluent, and alcohol. The admixture is then treated with CO to form the carbonate. Alternatively and preferably, the alkaline earth metal carbonate is formed by adding an alcoholic slurry of the alkaline earth metal basic compound to an admixture of the other materials. The total admixture is then treated with CO₂ to form the carbonate.

Suitable alcohols for use in the "one-step" process include C₁-C₁₀ alkanols, the monoether alcohols of ethylene glycol containing up to eight carbon atoms, and the monoether alcohols of diethylene glycol containing up to eight carbon atoms. Examples of suitable alcohols include methanol, ethanol, propanol, isobutanol, pentanol, hexanol, octanol, decanol, 2-methoxy ethanol, and 2-ethoxy ethanol. The preferred alcohols are the C₁-C₁₀ alkanols, with the C₁-C₃ alkanols being more preferred.

Process Conditions

In carrying out the one-step method, the oil soluble dispersing agent (whether pre-formed, or formed in situ), non-volatile diluent and alcohol-alkaline earth metal basic compound slurry are intimately admixed preparatory to carbonation. The water component of the mixture may be added at any time prior to the final controlled heating step, and may be added at different times in two or more increments, if desired. The same is true of any alcohol which is added in addition to that introduced with the slurry. In the case of the water, however, it is preferred to add the entire amount of water at the outset and prior to carbonation since thicker products appear to be yielded when this procedure is followed.

In carrying out the carbonation of the mixture to form the carbonate, about 1.5 moles of carbon dioxide must be introduced to the mixture for each mole of alkaline earth metal present. In addition, the gas necessary to complete carbonation (as described) must be introduced to the mixture within about 90 minutes in order to obtain the high viscosity grease-like product sought, and it is preferred that this amount be introduced at a sufficient rate to achieve completion of carbonation and formation of the complex within from 20 to 40 minutes.

The carbon dioxide required may be introduced into the mixture by blowing or bubbling the gas through the mixture, or by immersing dry ice in the mixture. The reaction is exothermic and its progress can be followed by observation of the change in temperature of the reaction mixture. It is preferred that the temperature be retained below about 50° C during carbonation.

Upon completion of carbonation, the mixture, which then contains the oil-soluble dispersing agent, the nonvolatile carrier material, and the alkaline earth metal carbonate resulting from carbonation is subjected to a controlled heating step. Between the carbonation procedure and the heating step, water and/or alcohol may be added to the mixture in order to bring the total content of these two components in the mixture up to that which has been hereinbefore described as the operative requirements in this respect. The heating step with which the one-step method is concluded is quite important, and the manner in which it is conducted determines whether the desired high consistency-low penetration grease-like compositions are yielded, or whether a fluid dispersion of the general type described in U.S. Pat. Nos. 2,956,018 and 2,861,951 to Carlyle and also in U.S. Pat. Nos. 3,150,088 and 3,027,325 to McMillen are formed.

In the final heating step of the process, two objectives are sought by the heating. First, the light solvents must be stripped from the mixture, except, perhaps, for small amounts of water and alcohol and such light hydrocarbon carrier material as it is desired to have remain in the final product for purposes of enhancing the ease of processing. Thus, the heating will remove substantially all of the alcohol and water which are not consumed in the grease producing reaction, and any very light hydrocarbon solvents, such as hexane, which are incorporated in the mixture in order to facilitate the carbonation of the alkaline earth metal base compound.

The second function of the heating is to supply the heat of reaction which is necessary to effect the conversion of the mixture to a high consistency grease-like composition.

To then describe the specific parameters which are critical in the heating of the heterogeneous mixture which exists after carbonation in order to form the described grease-like compositions, it is necessary that the mixture be heated to a temperature above about 50° C.

After reaching the threshold temperature of about 50° C for effecting the conversion reaction, it is then desirable to gradually increase the temperature of the reaction mixture to above 100° C, and preferably ultimately to about 160° C. This is because water in the mixture commences to be stripped or driven off at 100° C, and the total processing time becomes unacceptably long when temperatures exceeding this level are never attained during the final heating step. On the other hand, it is critical to the formation of the desired grease products that the temperature zone of 50° C to 100° C not be traversed too rapidly. The effect of increasing the temperature of the mixture at an excessive rate is to drive an excessive amount of the water from the mixture before it has had an opportunity to enter into the reaction necessary to convert the mixture to grease. From this it follows that the greater the amount of water in the mixture within the operative range of water content hereinbefore described, the higher may be the rate at which the temperature is raised from 50° C to 100° C.

A definite relationship exists between the amount of water in the heated mixture and the time required to traverse the temperature zone of from 50° C to 100° C. For example, where the minimum operative quantity of water is present in

the mixture at the inception of the final heating step (that is, 0.25 mole of water per mole of overbasing alkaline earth metal present), the time within which the mixture must be maintained between 50° C and 100° C is at least 4.5 hours. This time period decreases in a fairly regular uniform fashion as the amount of water present in the mixture with respect to the amount of alkaline earth metal present increases. Thus, when a water level of about 2.5 moles of water per mole of alkaline earth metal is reached, a time period of only about 45 minutes in the temperature range of 50° C to 100° C is required in order to effect the desired conversion to the grease-like product. At this and higher water levels, the time requirement to effect the desired conversion drops off very sharply so that the reaction mixture may be heated from 50° C to 100° C at as rapid rate as may be desired. This relationship between the transition time for elevating the temperature of the reaction mass from 50° C to 100° C in instances where the water content of the reaction mixture is in the range of from about 0.25 mole of water per mole of alkaline earth metal (present in an overbasing capacity) to about 2.5 moles of water per mole of the metal can be approximated by the expression:

$$t = 0.75 + 1.7 \times (2.5 - m)$$

where t equals the time in hours within which the mixture must be retained in the temperature range of between 50° C and 100° C, and m is the number of moles of water present in the mixture per mole of alkaline earth metal present in the mixture in an overbasing capacity.

Where the reaction mixture is heated too rapidly to above 100° C, the water appears to be stripped from the mixture too fast to permit the completion of reaction. The result then is that there is formed a homogeneous dispersion of alkaline earth metal carbonate which is quite fluid and is similar to the lubricating oil additives which are yielded by the processes described in U.S. Pat. Nos. 2,956,018 and 2,861,951 to Carlyle and also in U.S. Pat. No. 3,150,088 to Hunt.

The formation of the desired grease-like product is clearly evidenced by the marked and rapid change in the observable physical properties of the mixture. The most striking change, perhaps, is in the viscosity of the mixture, which increases rapidly as the conversion to grease-like product occurs. The grease-like product is tacky and opaque and is macroscopically homogeneous. It is highly basic in terms of its acetic base number. (This term is well-known in the art, being described in U.S. Pat. No. 3,150,088.)

As the starting mixture undergoes conversion or modification to yield the grease-like product, it will often be desirable to add a volatile solvent to the mixture in order to maintain its viscosity within a manageable range.

In the heating step, it is not necessary to remove all of the water and alcohol from the mixture, particularly where the product is to be used as a rust inhibitor.

It is to be understood that the one-step method of preparing the grease-like composition is not part of my invention. This method is disclosed and claimed in application Ser. No. 727,719 filed May 8, 1968.

The Polymer

The term polymer as used herein includes certain copolymers which meet the specified requirements. Suitable polymers for use in our invention have the following properties:

- a low degree of crystallinity; i.e., less than 50 percent, preferably less than 25 percent, crystallinity,
- a molecular weight in the range of from about 3,000 to about 1 million,
- a high solubility in predominantly aliphatic hydrocarbon solvents, such as hexane, n-decane, Stoddard solvent, kerosene and petroleum lubricating oils.

Polymers meeting the above-listed description are often termed atactic or amorphous.

Examples of suitable types of polymers include low molecular weight or low density polyethylene, amorphous polypropylene, polyisobutylene, polyterpenes; copolymers of the foregoing with vinyl monomers, such as vinyl chloride, and vinyl esters, such as vinyl acetate; polyacrylic acids, and polymethacrylic acids.

Specific examples of suitable polymers include the following:

Supplier	Tradename	Polymer Type
Dow	Zetafax	Ethylene-isobutyl acrylate copolymer
DuPont	Elvax	Ethylene-vinyl acetate copolymer
DuPont	Alathon	Low molecular weight polyethylene
Eastman	Eastobond	Polyolefin hot melt adhesive
Eastman	Epolene	Low molecular weight polyethylenes and amorphous polypropylenes
Goodyear	"Wing Tack"	Polyterpene
Neville	Nevillac	Phenol modified Coumaroneindene resin
Rohm and Haas	Acryloid	Polymethyl meth-acrylate
Kenrich	Kenflex	Synthetic thermoplastic resin from condensation of high boiling aromatics with Formaldehyde

Particularly suitable polymers include polyterpenes, amorphous polypropylenes, polyolefins, ethylene-isobutyl acrylate copolymers and ethylene-vinyl acetate copolymers. Preferred polymers are the polyterpenes, amorphous polypropylenes, low molecular weight polyethylenes, and ethylene-vinyl acetate copolymers.

Relative Amounts of Polymer and Thixotropic, Grease-Like Composition in Our Composition

Polymer	Parts by Weight Thixotropic Composition
Suitable	0.1-25
Preferred	0.2-10
	75-99.9
	90-99.8

Preparation of Blend of Polymer and Thixotropic, Grease-like Composition

No particular technique is required to prepare the blend of polymer and thixotropic, grease-like composition. This is particularly true since usually the amount of polymer used is relatively small. After adding the required amount of polymer to the thixotropic, grease-like composition, preferably slowly in incremental amounts, the admixture is stirred sufficiently to provide a homogeneous composition.

Application of the Composition to Metal Surfaces

The composition used in my invention can be applied "as is" to the metal surface, usually, by means of a brush. Preferably, the composition is diluted in a volatile solvent for application to the surface. The use of a volatile solvent provides a more uniform film on the metal surface and enables the use of a spray. The latter can reduce substantially the cost of applying the composition.

The nature of the volatile solvent used is not a salient feature of my invention, and it is believed those skilled in the art, without undue experimentation, can readily ascertain suitable solvents. Examples of suitable solvents include volatile hydrocarbon solvents, such as Stoddard solvent, kerosene, petroleum naphtha and the like. Also, certain nonflammable chlorohydrocarbons are suitable. For reasons of safety, it is preferable to use solvents having a flash point of at least 100° F and even higher. The amount of solvent is dependent on the particular method of application. Usually, a suitable amount of solvent is in the range of from about 40 to about 90 percent

by weight. Preferably, it is from about 50 to about 80 percent by weight.

The composition of my invention can be used as a primer on any type of metal surface which is to be coated with a conventional paint. Preferably it is used on metals which are subject to severe corrosion, such as ferrous metals.

A particular advantage of the composition used in my invention is that the metal surface requires little or no preparation prior to application. Many primers require that the surface be meticulously clean (e.g. by chemical cleaning or sand-blasting to white metal) prior to application. By contrast, the composition, used in my invention, when applied to rusted surfaces result in a satisfactory film. Usually, the surface is treated moderately, e.g. by scraping or brushing sufficiently to remove loose scale prior to application of the grease-like composition.

The amount of composition which is applied can be readily determined by those skilled in the art. A thicker film usually provides better protection but, obviously, is more expensive. A film having a thickness of about 2.5 mils has been found to be optimum with respect to both performance and economics.

The composition should be substantially solvent-free before applying the conventional paint. Usually, the composition is solvent-free in 18-72 hours.

Suitable Paints

A variety of conventional paints have been found to be satisfactorily applied over the composition used in my invention. Examples of suitable generic-type paints include the following:

- Amine cured epoxy (2 component)
- Polyamide cured epoxy
- Urethane (2 component)
- Alkyd enamel
- Phenolic enamel
- Acrylic water emulsion
- Vinyls (solvent or emulsion based)

Knowing that the composition described herein is satisfactory as a primer for conventional paints anyone skilled in this art can readily select a suitable paint for the outer surface. Similarly, the selection of a paint to provide optimum results can be made readily.

Advantages of My Invention

As indicated previously, a primary advantage of the use of the composition as a primer is that the metal surface requires little, or no, preparation prior to being coated with the composition.

Secondly, use of the composition as a primer provides an improved resistance to corrosion of metal surfaces.

Thirdly, use of the composition as a primer permits an increase in the thickness of a single-coat film, particularly with alkyd paints.

Fourthly, use of the composition as a primer results in a film which is harder, tougher and less tacky than the use of the composition of application Ser. No. 729,875 as a primer.

In order to disclose the nature of the present invention still more clearly, the following illustrative examples will be given. It is to be understood that the invention is not to be limited to the specific conditions or details set forth in these examples except insofar as such limitations are specified in the appended claims. Unless stated otherwise, all parts stated are by weight.

EXAMPLE 1

This example illustrates the reduction in tackiness of the polymer-thixotropic, grease-like composition as compared to the thixotropic, grease-like composition alone.

The thixotropic grease-like composition was prepared using the "one-step" method described hereinbefore.

The sulfonic acid solution employed contained 27 percent (by wt.) mixed sulfonic acids, 60 percent (by wt.) n-hexane

and 13 percent (by wt.) nonvolatile mineral oil (pale oil). The mixed sulfonic acids contained 70 percent (by wt.) oil-soluble sulfonic acids derived from "dimer alkylate" and 30 percent (by wt.) oil-soluble sulfonic acids derived from "NAB" Bottoms. Both "dimer alkylate" and "NAB" Bottoms have been described in the foregoing.

The following materials were added to a 12-liter flask:

- 2,000 parts Stoddard solvent
- 15 parts water
- 1,582 parts sulfonic acid solution

To the above-listed admixture was added a slurry of the following:

- 345 parts $\text{Ca}(\text{OH})_2$
- 1,587 parts methanol

While stirring the resulting admixture it was blown with CO_2 . Using a large flow meter, with a reading of 10, (approximately 9,250 cc's/minute) it was blown with CO_2 until the temperature peaked. Then the rate of blowing was reduced to a meter reading of 5 and continued for 15 minutes. The time-temperature data for the CO_2 blowing were as follows:

Begin CO_2	28° C.
After 5 min.	36° C.
After 10 min.	48° C.
After 11 min.	49° C.
After 12 min.	51° C. (peak)
Following peaking	
5 min.	44° C.
10 min.	40° C.
15 min.	36° C.

The carbonated admixture was then heated to reflux temperature (67° C) and maintained at this temperature for 15 minutes.

The carbonated admixture was cooled to about 55° C, whereupon 140 parts water were added over a 15-minute period.

The resulting admixture was heated to reflux temperature and maintained at this temperature for 15 minutes.

The admixture was then heated slowly to a temperature of 160° C. to remove the lower boiling solvents.

The yield of product was 2,720 parts.

To the product was added 700 parts Stoddard solvent to product a final product of 3,420 parts.

The final product had the following composition:

- 12.2 percent Calcium sulfonate
- 12.2 percent Calcium carbonate*(*Acetic base number=137)
- 9.1 percent 100 Pale oil
- 66.5 percent Stoddard solvent

Various polymers were added to the product at a concentration of 1 to 5 weight percent based on the nonvolatile content. Blending of the polymer and thixotropic, grease-like product was obtained by adding the polymer to the heated (80° to 150° C) product, described above, and stirring until all of the polymer dissolved. The nature of the various polymers used is shown in Table I.

In order to evaluate the tackiness of the various compositions (thixotropic, grease-like composition plus polymer), a solution of the compositions were applied to steel "Q" panels. Upon evaporation of the volatile solvent, a film of the composition (thixotropic, grease-like composition plus polymer) formed on the panels. The films of the various compositions were evaluated for tackiness with an Instron machine using the following procedure. A brass plunger, 0.500 inch in diameter and weighing 243.5 grams was lowered onto the surface of a coated panel and its weight allowed to rest on the panel for about 30 seconds. Then the plunger was lifted from the panel. A surface with no tackiness or adhesiveness would require a force of 243.5 grams to lift the brass plate off the surface. The amount of force required, in excess of 243.5 grams, to lift the brass weight was a measure of the tackiness of the coated surface.

The nature of the polymers tested and the excess force data are shown in Table I.

TABLE I

Instron Test Measurement of Tackiness of Coatings

Composition	Film Thickness Mils	Excess Force Grams*
Thixotropic, Grease-like Composition alone (TGC)	7.3	72.4±13
TGC+5% "Nevillac" 10 (1)	7.3	38.7±12
TGC + 5% "Eastobond" M-3 (2)	2.5	27.3±10
TGC + 5% "Acryloid" 917 (3)	2.5	54.8±9
TGC + 5% "Kenflex" A (4)	2.0	5.8±1
TGC + 5% "Epolene" D-11 (5)	4.6	14.3±3
TGC + 5% "Zetafax" 1278 (6)	3.4	6.5±1
TGC + 5% "Zetafax" 1275 (6)	5.3	10.9±3
TGC + 2% "Epolene" C-16 (7)	2.4	16.7±6

*Lower values indicate improved performance.

- (1) A phenol modified coumarone-indene resin from Neville Chemical Company.
 (2) A polyolefin based hot melt adhesive resin from Eastman Chemical Products, Inc.
 (3) A polymethyl methacrylate from Rohm and Haas Company
 (4) A synthetic thermoplastic resin from condensation of high boiling aromatics with formaldehyde from Kenrich Petrochemicals, Inc.
 (5) An amorphous polypropylene from Eastman Chemical Products, Inc.
 (6) An ethylene-isobutyl acrylate copolymer from Dow Chemical Co.
 (7) A low molecular weight polyolefin from Eastman Chemical Products, Inc.

EXAMPLE 2

This example illustrates the improved mechanical performance of a conventional paint over the composition of my invention as compared to the composition of application Ser. No. 729,875.

The following compositions were tested:

A — the composition of Ser. No. 729,875

B — the thixotropic, grease-like composition of Example 1 — similar to A but containing less nonvolatile diluent oil

C — Composition B plus 3 percent "Eponlene" C-16

D — Composition B plus 5 percent "Eastobond" M-5W (amorphous polypropylene)

Films of the compositions were cast on 4 in. × 8 in. mild steel "Q" panels. The coated panels were painted over with a conventional white alkyd enamel. It was noted that the coatings from compositions C and D accepted the paint top coat more readily and covered more smoothly than did the coatings from compositions A and B. The alkyd enamel top coat was dry in 24 hours over all the compositions.

The coatings were subjected to adhesion and abrasion resistance tests. Adhesion was evaluated by a "scotch tape" test. In this test a grid ¼ in. × ¼ in. was cut through the coating down to bare metal. The grid consisted of 7 lines ¼ in. apart intersected at right angles by another 7 lines at ¼ in. spacing. A ¼ in. wide strip of "Scotch" magic transparent tape was placed over the grid and pressed firmly in place with a finger. Then the tape was lifted, quickly and smoothly. The number of squares, out of the total of 36, in which the coating separated from the metal and adhered to the tape was counted. A lower value in this test indicates improved results.

The abrasion resistance was measured by determining the amount of force that must be applied to 1 square inch of No. 100 grit sandpaper being pulled over the surface of the coating before bare metal is revealed. In this test a higher value indicates improved results.

The results of the test in this example are shown in Table II.

TABLE II

Adhesion and Abrasion Tests of Coatings

Thick- Topcoat	Thickness Mils	Primer	ness Mils	Adhesion Test	Abrasion Test
White alkyd enamel	3.2±0.3	None	0	15	>14
White alkyd					

enamel	~3	Comp. A	2.58±0.08	21	~6
White alkyd enamel	— 3	Comp. B	3.19±0.13	8	~7½
White alkyd enamel	~3	Comp. C	3.91±0.17	1	~10
White alkyd enamel	~3	Comp. D	4.37±0.16	0	~9

EXAMPLE 3

This example shows the improvement obtained when using the primer of my invention (which contains a minor amount of polymer) as compared to the composition of U.S. Pat. No. 3,384,586 (which contains a major amount of polymer) when the latter is used as a primer.

The thixotropic, grease-like composition was prepared using the "two-step" method.

The colloidal dispersion of calcium carbonate used as a starting material had the following composition:

30 percent calcium sulfonate

43 percent nonvolatile diluent (170 pale oil)

27 percent calcium carbonate* (*The material had an acetic base number of about 300.

To a 10-quart Hobart mixer bowl were added 6,000 parts of the colloidal dispersion of calcium carbonate. The material was heated to 150° F whereupon the following were added:

600 parts water

30 parts methoxy ethanol

The admixture was heated slowly to 200° to 210° F and then heated. The total time of heating from 150° to 210° F was about 1 hour. The solvents were removed by heating to 315° F using a reduced pressure (partial house vacuum).

The resulting product was a thixotropic, grease-like composition having an ASTM penetration of 133 at 77° F.

Using a planetary type grease mixer the following compositions were prepared:

Composition A — parts

78.4 Stoddard solvent

53.4*(*This composition is typical of U.S. Pat. No. 3,384,586.)

90 polyvinyl chloride

34 dioctyl phthalate

10 TGC**(**Thixotropic, grease-like composition prepared in this example.)

Composition B — parts

61.4 Stoddard solvent

38.6*(*This composition is comparative to U.S. Pat. No. 3,384,586 and illustrates the properties of a composition containing a minor amount of polymer.)

10 polyvinyl chloride

3.8 dioctyl phthalate

90 TGC

Using a Waring blender the following compositions were prepared:

Composition C — parts

105.5 Stoddard solvent

70.3 of:

90 polyterpene resin ("Wing Tack" 95)

10 TGC

Composition D — parts

60.9 Stoddard solvent

39.1 of:

10 polyterpene resin ("Wing Tack" 95)

90 TGC

Composition E — parts

61.7 Stoddard solvent

38.3 TGC

The viscosity characteristics of the above-described compositions are shown in Table III.

TABLE III

Brookfield Viscosity at

Composition	Wt. % Non-volatile	12 RPM	77° F. No. 2 Spindle, cps.	
			30 RPM	Ratio
A	40.5	311	148	2.10
B	38.6	467	275	1.70
C	40.0	<25	<10	—
D	39.1	611	317	1.93
E	38.3	1016	522	1.95

The data listed above shows that blends containing a large amount of thixotropic, grease-like compositions (e.g. B and D) have a much higher viscosity than do blends containing a small amount of thixotropic, grease-like composition (A and C).

EXAMPLE 4

This example shows the film properties of various compositions similar to those described in Example 3. The compositions were the same with the exception that the amount of Stoddard solvent was different in Compositions A and C. In these compositions the amount of Stoddard solvent was as follows:

Composition A — 46.6 parts

Composition B — 29.7 parts

A panel was dipped in the composition. After allowing the solvent to evaporate the film was measured and the coated panel was evaluated. The results are shown below:

TABLE IV

	Compositions				
	A	B	C	D	E
Dip Film, Thickness, mils	5.93	2.45	3.00	2.77	3.64
Film properties:					
Appearance					
and Feel	Opaque, white, soft	Tan, translucent, tacky,	Tan, transparent, hard, brittle	Tan, transparent, flexible, slightly tacky	Tan, transparent, flexible, tacky
Paint Adhesion	Poor	Good	Very Poor	Very Good	Good

EXAMPLE 5

This example shows the performance as primer of the compositions described in Example 4. First, the steel panels were coated with the compositions as a primer; then they were coated with a white alkyd enamel. The panels were evaluated in the ASTM B-117 Salt Fog Test after 100 hours exposure. The results are shown in Table V.

EXAMPLE 6

This example illustrates another variation of the one-step

method of preparing the colloidal dispersion of calcium carbonate, which is used to prepare the thixotropic, grease-like composition.

The methoxy ethanolic solution of Ca methoxy ethoxide was prepared in accordance with the procedure described in U.S. Pat. No. 3,150,088.

The sulfonic acid solution employed in this example contained 27 percent (by wt.) mixed sulfonic acids, 60 percent (by wt.) n-hexane and 13 percent (by wt.) nonvolatile mineral oil (pale oil). The mixed sulfonic acids contained 60 percent (by wt.) oil-soluble sulfonic acids derived from "dimer alkylate" and 40 percent (by wt.) oil-soluble sulfonic acids derived from "NAB" Bottoms. Both "dimer alkylate" and "NAB" Bottoms have been described in the foregoing.

To a one-liter flask were added:

150 g. — sulfonic acid solution

49 g. — 100 pale oil

The admixture was heated to 35° C and the sulfonic acid was neutralized by adding 31 grams of a methoxy ethanolic solution of Ca methoxy ethoxide-carbonate, containing 6.95 percent Ca. The temperature was adjusted to 40° C and the following solutions were added concurrently at constant rates:

252 g. — methoxy ethanolic solution of Ca methoxy ethoxide-carbonate (containing 6.95 percent Ca)

59.4 g. — solution containing:

29.3 percent methoxy ethanol

14.2 percent methanol

56.5 percent water

After the addition, the admixture was heated at reflux temperature for 5 hours. Then 170 grams of Stoddard solvent were added and the major portion of the solvents were removed by heating to 150° C.

Removal of the Stoddard solvent from a portion of the product resulted in a thixotropic, grease-like composition having an ASTM penetration of 187.

The invention having thus been described, what is claimed and desired to be secured by Letters Patent is:

1. A method of improving resistance to corrosion of metal surfaces wherein the method comprises:

A. applying to the metal surface a primer composition which comprises, in parts by weight:

1. from about 75 to about 99.9 parts of a thixotropic, grease-like composition consisting essentially of:

i. from about 2 to about 80 parts nonvolatile diluent selected from the group consisting of mineral lubricating oils, synthetic lubricating oils, and petroleum waxes,

ii. from about 5 to about 55 parts oil-soluble dispersing agent,

iii. from about 1 to about 45 parts alkaline earth metal carbonate, said grease-like composition being characterized further in that it has an acetic base number of at least 50, does not flow at 210° F, and has a dropping point of at least 480° F

2. from about 0.1 to about 25 parts polymer, said polymer being characterized as having a crystallinity of less than 50 percent, a molecular weight in the range of from about 3,000 to about 1 million and a high solubility in predominantly aliphatic hydrocarbon solvents,

TABLE V

Composition:	Film thickness, mils		Edge corrosion	Corrosion in "X" score ¹	Creepage from score, mm.	Rust or inner surface, 3" x 7" test	Approx. area, percent rusted ²	Rust ratings ³	
	Comp.	Paint topcoat						Mil-C 83933	ASTM D-1654-61
A	1.58	1.5	Severe	Very severe	~1	Light	<5	Fail	8
B	1.23	1.5	Light ⁴	Very light	None	None	<1	Pass	9
C	1.8	1.5	Severe	Severe	~2	Light	<5	Fail	8
D	1.22	1.5	Light ⁴	Light	None	None	<1	Pass	9
E	1.38	1.5	do. ⁴	do.	None	do.	0	do.	9+
Unprimed control panels		1.5	Moderate	Severe	~2	Light	~10		

¹ In this test an "X" is cut through the coatings to the metal. Then the scored panel is subjected to the salt fog test.

² Rating of unscored panel, ignoring a 1/2 inch wide border around the edges.

³ Rating of unscored panels.

⁴ Top edge.

- B. allowing the coated metal surface to become substantially free of any volatile solvent which may be present, and
- C. applying to the coated metal surface a conventional paint wherein said paint adheres to said primer.
2. The method of claim 1 wherein the oil-soluble dispersing agent is a sulfonic acid, or a metal salt thereof.
3. The method of claim 2 wherein the alkaline earth metal carbonate is calcium carbonate.
4. The method of claim 3 wherein the polymer is selected from the group consisting of polyterpenes, amorphous polypropylenes, low molecular weight polyethylenes, and ethylene-vinyl acetate copolymers.
5. The method of claim 4 wherein the conventional paint is selected from the group consisting of two-component amine cured epoxy, two-component urethane, alkyd enamel, phenolic enamel, acrylic water emulsion, and vinyl.
6. The method of claim 5 wherein the polymer is a polyterpene.
7. The method of claim 5 wherein the polymer is an amorphous polypropylene.
8. The method of claim 5 wherein the polymer is a low molecular weight polyethylene.
9. The method of claim 5 wherein the polymer is an ethylene-vinyl acetate copolymer.
10. A method of improving resistance to corrosion of metal surfaces, wherein the method comprises:
- A. applying to the metal surface a primer composition which comprises, in parts by weight:
- i. from about 90 to about 99.8 parts of a thixotropic, grease-like composition consisting essentially of:
 - i. from about 20 to about 70 parts nonvolatile diluent selected from the group consisting of mineral lubricating oils, synthetic lubricating oils and petroleum waxes,
 - ii. from about 6 to about 35 parts calcium salt of an oil soluble sulfonic acid,
 - iii. from about 5 to about 30 parts calcium carbonate, said grease-like composition being characterized further in that it has an acetic base number of at least 50, does not flow at 210° F, and has a dropping point of at least 480° F,
 2. from about 0.2 to about 10 parts polymer, said polymer being characterized as having a crystallinity of less than 50 percent, a molecular weight in the range of from about 3,000 to about 1 million and a high solubility in predominantly aliphatic hydrocarbon solvents,
- B. allowing the coated metal surface to become substantially free of any volatile solvent which may be present, and
- C. applying to the coated metal surface a conventional paint wherein said paint adheres to said primer.
11. The method of claim 10 wherein the nonvolatile diluent is a mineral lubricating oil.
12. The method of claim 11 wherein the polymer is selected from the group consisting of polyterpenes, amorphous polypropylenes, low molecular weight polyethylenes, and ethylene-vinyl acetate copolymers.
13. The method of claim 12 wherein the polymer is a polyterpene.
14. The method of claim 12 wherein the polymer is an amorphous polypropylene.
15. The method of claim 12 wherein the polymer is a low

- molecular weight polyethylene.
16. The method of claim 12 wherein the polymer is an ethylene-vinyl acetate copolymer.
17. The method of claim 12 wherein the conventional paint is selected from the group consisting of two-component amine cured epoxy, two-component urethane, alkyd enamel, phenolic enamel, acrylic water emulsion, and vinyl.
18. The method of claim 17 wherein the polymer is a polyterpene.
19. The method of claim 17 wherein the polymer is an amorphous polypropylene.
20. The method of claim 17 wherein the polymer is a low molecular weight polyethylene.
21. The method of claim 17 wherein the polymer is an ethylene-vinyl acetate copolymer.
22. A method of coating a substrate which comprises:
- A. applying to the substrate a primer composition which comprises in parts by weight:
1. from about 75 to about 99.9 parts of a thixotropic, grease-like composition consisting essentially of:
 - i. from about 2 to about 80 parts nonvolatile diluent selected from the group consisting of mineral lubricating oils, synthetic lubricating oils, and petroleum waxes,
 - ii. from about 5 to about 55 parts oil-soluble dispersing agent,
 - iii. from about 1 to about 45 parts alkaline earth metal carbonate, said grease-like composition being characterized further in that it has an acetic base number of at least 50, does not flow at 210° F, and has a dropping point of at least 480° F,
 2. from about 0.1 to about 25 parts polymer, said polymer being characterized as having a crystallinity of less than 50 percent, a molecular weight in the range of from about 3,000 to about 1 million and a high solubility in predominantly aliphatic hydrocarbon solvents,
- B. allowing the coated substrate to become substantially free of any volatile solvent which may be present, and
- C. applying to the coated substrate a conventional paint wherein said paint adheres to said primer.
23. A metal article, one surface of which has been coated with a primer composition and a conventional paint adhered to said primer, said primer composition comprising in parts by weight:
1. from about 75 to about 99.9 parts of a thixotropic, grease-like composition consisting essentially of:
 - i. from about 2 to about 80 parts nonvolatile diluent selected from the group consisting of mineral lubricating oils, synthetic lubricating oils, and petroleum waxes,
 - ii. from about 5 to about 55 parts oil-soluble dispersing agent,
 - iii. from about 1 to about 45 parts alkaline earth metal carbonate, said composition being characterized further in that it has an acetic base number of at least 50, does not flow at 210° F, and has a dropping point of at least 480° F,
 2. from about 0.1 to about 25 parts polymer, said polymer being characterized as having a crystallinity of less than 50 percent, a molecular weight in the range of from about 3,000 to about 1 million and a high solubility in predominantly aliphatic hydrocarbon solvents.

* * * * *