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2,455,854

STRIPPABLE COATING COMPOSITION COMPRISING A POLYCHLOROPRENE AND ALUMINUM POWDER

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This invention relates to coating compositions and more particularly to sprayable coating compositions which adhere to metal surfaces only slightly when applied thereto and dried, thus permitting stripping of the coating from such surfaces when desired.

The export of vast quantities of metal articles of manufacture, particularly war equipment for Allied Armed Forces, has created an urgent need for a means for temporarily protecting such material from the corrosive effects of the elements during transportation and storage prior to actual use of such equipment. Proper protection will also be needed for post-war export of products manufactured for peaceful purposes.

Transoceanic shipping because of exposure to salt water is particularly destructive and the tropical and arctic climates in those parts of the world where such material is sent are also highly detrimental to unprotected metal surfaces.

In many instances a permanent protective coating is not permissible, for example, on mechanical replacement parts, and for such purposes any coating which is originally applied must be capable of being readily stripped from the metal surface before the article is put to its intended use. Even when an article is finished with a permanent protective and decorative coating, it is sometimes desired to further temporarily protect this finish against mechanical scuffing and abrasion encountered during shipping and storage handling. Thus, a temporary readily strippable coating applied over the permanent finish insures the final consumer receiving the article in an un-marred condition. Coatings of this type applied by hot dipping methods have been partially successful but are limited in their utility to relatively small units.

This invention has as an object the provision of a coating composition which has low adherence to metal surfaces when dried whereby the film may be readily stripped from the surface even after extended storage periods. Another object is the provision of a strippable coating composition which is waterproof, tough and resilient and which has excellent flexibility at very high and low temperatures. Another object is the provision of a strippable coating composition which affords a film that has good tensile strength and distensibility. Another object is the provision of a strippable coating composition which may be applied by spraying. Another object is the provision of a strippable coating composition which has good resistance to the passage of water vapor. Another object is the provision of a coating composition which may be stripped from permanent decorative and protec-

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tive synthetic resin finishes (for example, alkyd resin finishes) cellulose derivative and varnish type finishes when thoroughly dried. Another object is the provision of a strippable coating composition which is resistant to volatile aliphatic hydrocarbon oils and greases. Another object is the provision of a strippable coating composition which has good durability on outdoor exposures even in the most severe climatic conditions such as encountered in the tropics and in the far north. Another object is the provision of a strippable coating which reflects rather than absorbs light and heat, thus contributing materially to improved durability of the coatings on extended outdoor exposures. A further object of the invention is the provision of a strippable coating which does not develop increased adhesion to metal surfaces during extended storage periods. A further and important object of the invention is the provision of a strippable coating composition which affords excellent resistance to corrosion of a metal substrate when exposed to the elements including the particularly adverse conditions encountered during transoceanic shipping and extended storage at locations near salt water. A still further object is the provision of a strippable coating which has low surface tack after evaporation of the volatile solvents thus preventing "blocking" when the coated surfaces are placed in direct contact. A still further object is the provision of a strippable coating which has a modulus of elasticity such that ease of stripping is thereby facilitated. Other objects will become apparent as the description of the invention proceeds.

These objects are accomplished in accordance with the present invention by means of a sprayable coating composition having low adherence to metal surfaces containing a sulfur-neoprene (polymerized sulfur modified chloroprene) and a metal powder, such as finely divided aluminum powder. In the preferred embodiment of the invention, there is included also an "auxiliary stripping agent" selected from the group consisting of soya lecithin, lead soap of petroleum oil acids and a stearyl alcohol ester of styrene-maleic anhydride interpolymers.

Therefore, the term "auxiliary stripping agent," as used herein, means any one of the above referred to materials; i. e., soya lecithin, a lead soap of petroleum oil acids, or a stearyl alcohol ester of a styrene-maleic anhydride interpolymers.

The following examples are given by way of illustration only and no limitations are intended thereby except as indicated in the appended claims.

Example 1

	Per cent by weight
Neoprene KNR (polymerized sulfur modified chloroprene)-----	17.80
Plasticizer-stabilizer (Du Pont #552 accelerator ¹)-----	.21
Phenyl-b-naphthylamine (anti-oxidant)-----	.36
Stearic acid-----	.36
Calcined magnesia (extra light)-----	.72
Zinc oxide-----	.18
Toluene-----	34.65
Xylene-----	34.60
Mineral spirits-----	3.72
Aluminum powder-----	7.40
	100.00

¹ Piperidinium pentamethylene dithiocarbamate.

The KNR neoprene used in the compositions of this invention consisted of a type having sulfur in chemical combination with the polychloroprene, made by polymerizing chloroprene (2 chloro-1,3 butadiene) in the presence of elementary sulfur as fully described in U. S. Patent 2,351,735.

The aluminum powder which is present in the proportion by weight of about 41.5 parts of aluminum powder to 100 parts of KNR neoprene was added in the form of a previously prepared paste consisting of finely divided aluminum powder in mineral spirits in the proportion of 66.5 parts by weight of aluminum powder to 33.5 parts by weight of mineral spirits. A suitable compound of this type which is commercially available is known as Alcoa Albron paste #205 manufactured by the Aluminum Company of America. The paste should be added just prior to the incorporation of the accelerator and activator and just before it is desired to apply the coating in order to avoid any tendency toward gelation.

In preparing this composition, the KNR neoprene is dissolved in the toluene and xylene together with the plasticizer-stabilizer in an agitator mixer. A portion of this base is then ground in a ball mill for 16 hours with the magnesium and zinc oxides, stearic acid and anti-oxidant with pebbles in the ratio of 1½ parts by weight of pebbles to 1 part by weight of mill charge. This mill base is then added to the remainder of the KNR neoprene, stabilizer-plasticizer solution and agitated until a homogeneous mixture is secured.

In order to properly cure the coating it is necessary to add an accelerator (Du Pont #833—a butyraldehyde-mono-butylamine condensation product) in an amount of 0.8 part by weight and an activator (a litharge slurry consisting of 47.6% litharge and 52.4% xylene) in an amount of 7.2 parts by weight for each 100 parts by weight of the composition of Example 1 before application to the metal surface.

Some thickening was observed when the curing accelerator and activator were added which gradually disappeared within about 2-3 hours when the composition returned to the normal spraying viscosity noted above.

Two applications of the treated composition were then sprayed on polished steel panels with ½ hour drying time between coats to give a final dry film thickness of about 8 mils. One gallon of this composition will cover approximately 290 square feet of surface area at a thickness of one mil. The equipment used in applying the coating consisted of a De Vilbiss MBC type spray gun with an FF tip and a #704 "hot spray" type head. An air pressure of 90 pounds on the line and 20

pounds on the spray pot was used. However, the other types of conventional spray equipment can be used effectively also.

The coating was allowed to dry for about 20 hours to remove volatile solvents and then vulcanized by heating at 150° F. for 24 hours.

The composition was then readily stripped from the steel surface. The excellent resistance to corrosion which characterized this product is shown by the results obtained after ten consecutive cycles of exposures as follows:

16 hours at 100% relative humidity at 100° F.
3 hours at -40° F.
2 hours at 160° F.
3 hours immersion in a 5% salt solution at 70° F.

No corrosion or rusting on the polished steel surface substrate was observed.

The tensile strength of a film from this example with a thickness of 8 mils was 681 pounds per square inch and the modulus of elasticity at 100% elongation was 517 pounds per square inch.

Example 2

	Per cent by weight
Neoprene KNR (polymerized sulfur modified chloroprene)-----	18.20
Plasticizer-stabilizer (Du Pont #552 accelerator)-----	.22
Phenyl-b-naphthylamine (anti-oxidant)-----	.36
Stearic acid-----	.36
Calcined magnesia (extra light)-----	.72
Zinc oxide-----	.18
Toluene-----	35.46
Xylene-----	35.41
Mineral spirits-----	3.04
Aluminum powder-----	6.05
	100.00

This composition which contains aluminum powder in proportion by weight of about 33.3 parts of aluminum powder to 100 parts of KNR neoprene was prepared in accordance with the procedure of Example 1, including the addition in the same amount of the accelerator and activator. The final curing cycle was likewise the same as described above.

The coating was also readily stripped from the steel surface substrate and corrosion resistance when tested as shown for Example 1 was excellent.

Films 8 mils in thickness prepared from this composition had tensile strengths of 810 pounds per square inch and modulus of elasticity at 100% elongation of 506 pounds per square inch.

Example 3

	Per cent by weight
Neoprene KNR (polymerized sulfur modified chloroprene)-----	17.40
Plasticizer-stabilizer (Du Pont #552 accelerator)-----	.21
Phenyl-b-naphthylamine (anti-oxidant)-----	.35
Soya lecithin-----	.35
Stearic acid-----	.35
Calcined magnesia (extra light)-----	.68
Zinc oxide-----	.17
Toluene-----	33.55
Xylene-----	33.90
Mineral spirits-----	4.34
Aluminum powder-----	8.70
	100.00

This example differs essentially from Examples 1 and 2 in that a surface active agent is added whereby ease of stripping is facilitated. The composition contains aluminum powder in the proportion by weight of 50.0 parts of aluminum powder to 100 parts of KNR neoprene.

The procedure for the preparation of this composition, the addition of the accelerator and activator and the curing cycle was the same as for Example 1.

The coating was characterized by superior stripping properties. No corrosion or rusting was observed when a polished steel panel coated with this composition was subjected to the cycle of severe exposure conditions described above.

Films 8 mils in thickness prepared from the Example 3 composition had a tensile strength of 560 pounds per square inch and a modulus of elasticity at 100% elongation of 350 pounds per square inch.

Example 4

	Per cent by weight
Neoprene KNR (polymerized sulfur modified chloroprene)-----	17.80
Plasticizer-stabilizer (Du Pont #552 accelerator)-----	.21
Phenyl-b-naphthylamine (anti-oxidant)---	.36
Soya lecithin-----	.36
Stearic acid-----	.36
Calcined magnesia (extra light)-----	.72
Zinc oxide-----	.18
Toluene-----	34.29
Xylene-----	34.60
Mineral spirits-----	3.72
Aluminum powder-----	7.40
	100.00

This composition which contains soya lecithin, a surface active agent to facilitate ease of stripping and aluminum powder in the proportion of about 41.5 parts by weight of aluminum powder to 100 parts by weight of sulfur-neoprene was prepared in accordance with the procedure of Example 1. The amounts of accelerator and activator added and the curing cycle were likewise the same as shown for Example 1.

The coating was characterized by superior stripping properties. No corrosion or rusting was observed when a polished steel panel coated with this composition was subjected to the cycle of severe exposure conditions previously described.

Films 8 mils in thickness prepared from the Example 4 composition had tensile strengths of 828 pounds per square inch and modulus of elasticity at 100% elongation of 336 pounds per square inch.

Dry films of the compositions of the present invention are further characterized by very low water vapor permeability for example a film 8 mils thick prepared from the Example 1 composition had a water vapor permeability of but 35 grams per 100 square meters per hour at 39.5° C. under a vapor pressure differential corresponding to 100% relative humidity on one side of the film and less than 3% on the other side as determined in accordance with the procedure described in the "Paper Trade Journal" of October 3, 1935, pages 31-39.

As previously indicated, the new compositions must be vulcanized or cured in order to obtain the optimum results in the final film properties. This is preferably accomplished by heating for example at about 150° F. for about 24 hours.

Similar results may be secured by allowing the coating to cure in the air at room temperatures for a period of about 4 to 6 weeks. However, the unusually low water vapor transmission and the high degree of corrosion-resistance are apparent as soon as the volatile solvents are evaporated from the coating. It is also possible to strip the film from the metal substrate surface after about 48 hours at room temperature but for optimum results curing at elevated temperatures or for extended periods at room temperature is preferred.

The compositions are stable in storage over extended periods but following the incorporation of the accelerator and activator, the mixture should be used in less than 100 hours.

For satisfactory strippability the thickness of the dry film on the metal substrate surface should not be substantially less than about 4-5 mils and for adequate corrosion-resistance the film thickness should not be substantially less than about 7-9 mils. Somewhat greater thickness can be used and will give proportionately better protection, but it is not necessary and is undesirable economically.

Pigmentation of the compositions with aluminum powder affords improved outdoor durability particularly because it imparts to the coating the property of reflecting light and heat thus greatly reducing the deteriorating effects of such destructive factors which normally contribute greatly to coating failures where heat and light absorption are not counteracted.

For best results the aluminum powder is used in the proportion of about 40 parts by weight of aluminum powder to 100 parts by weight of sulfur-neoprene. Proportions of between about 15 parts and 50 parts by weight of aluminum powder to 100 parts by weight of sulfur-neoprene may be used with acceptable results. Smaller amounts of the aluminum powder tend to lower water-resistance and to increase film tack, thus causing undesirable blocking in the final film when coated surfaces are placed together. Substantially larger amounts of pigment decrease tensile strength and distensibility.

The plasticizer-stabilizer, preferably consisting of Du Pont accelerator #552, shown in the examples is added preferably in an amount of about 1.2% by weight based on the sulfur-neoprene content although satisfactory results are obtained when this material is included in an amount of between about 0.4% and 2.6%.

Zinc oxide when used in conjunction with magnesia improves the physical properties of the vulcanized neoprene. In addition, these ingredients which are preferably added in an amount of about 5% based on the sulfur-neoprene content, have been found to increase the water-resistance and corrosion-resistance of the neoprene coating. This may be due to their action in neutralizing any small quantities of hydrogen chloride that may be evolved during the curing period or when the films are exposed to sunlight or serious oxidizing conditions.

The stearic acid which is preferably included in an amount of about 2% based on the sulfur-neoprene reduces the time required for the sprayed film to reach the tack-free stage (usually about 16 hours) by some exudation to the surface and also appears to contribute to making the film more readily strippable.

In order to properly cure the sprayed film it is necessary to add an accelerator, such as Du Pont accelerator #833, a butyraldehyde-mono-

butylamine condensation product preferably to the extent of about 4% based on the sulfur-neoprene content of the composition. The action of this accelerator is augmented by the addition of preferably about 36% based on the sulfur-neoprene content of a 47.6% litharge slurry in xylene. In general, the accelerator may be used in an amount of between about 2% and 8% based on the sulfur-neoprene. If less than 2% is employed, curing at room temperature is poor and if the amount used is more than about 8% the stability of the composition is undesirably reduced and there is no improvement in the room temperature vulcanization rate. The litharge slurry used in conjunction with the accelerator may be added in an amount of between about 18% and 72% based on the sulfur-neoprene content. Amounts less than 18% fail to provide improved curing rates and when the content of the activator is increased above about 72%, there is a decided reduction in stability of the composition. The addition of these materials is particularly essential if the coating is to be cured at room temperature.

A very considerable number of different types of materials were tested as to their efficacy in promoting "strippability" properties, but with the exception of those agents previously described, namely, soya lecithin, lead soap of petroleum oil acids (known as Stoprust D-1 and manufactured by the Union Oil Company of California) and a stearyl alcohol ester of a styrene-maleic anhydride interpolmer which may be substituted directly for the soya lecithin in Examples 3 and 4, they were found to fail in one or more of the properties necessary to provide the desired results. The stearyl alcohol ester of a styrene-maleic anhydride interpolmer may be obtained by first preparing the styrene-maleic anhydride interpolmer in accordance with the procedures described in U. S. Patents 2,205,882 and 2,207,398. The polycarboxylic acid thus prepared may then be partly esterified by reacting with stearyl alcohol. The amount of alcohol should be less than that required for complete esterification of the polymeric carboxylic acid. The esterification may be carried out in the presence of a solvent such as an aromatic hydrocarbon. Soya lecithin, a colloidal material consisting of about 65% phosphatides and 35% soya bean oil is particularly adapted for use in the present compositions because of the improved "strippability" and resistance to corrosion which it imparts to the coating. For most purposes, therefore, it is much preferred. Although the use of an "auxiliary stripping agent" affords greater ease of stripping and is preferred, acceptable results are obtained without the addition of such agents as shown in Examples 1 and 2.

The "auxiliary stripping agent" of the type just described may be used in an amount of between about .05% and 5.0% by weight based on the sulfur-neoprene content of the composition in order to promote stripping of the dry film when desired. If the amount added is substantially less than .05% undesirable adherence to the metal surface substrate is observed and this tendency becomes more pronounced during extended storage periods. If the amount is increased much above 5.0%, the adhesion to the metal substrate surface is decreased beyond the desirable point so that the film is liable to come free prematurely. The optimum amount of "auxiliary stripping agent" is about 2% based on the sulfur-neoprene content.

The property of ready strippability of the improved coatings was found to be retained over considerable periods (for 3 months and more on outdoor exposures in Florida) with little or no tendency to develop undesirable adherence to the metal substrate surface. The tough, resilient, flexible character of the film provides protection from mechanical damage, scuffing and abrasion. The durability of the coating on severe outdoor exposures is excellent.

The KNR type of neoprene (sulfur-modified chloro-2-butadiene 1,3) shown in the example is a particularly desirable form of neoprene for the present purposes, because of its low viscosity characteristic, thus permitting higher solids in sprayable compositions, absence of webbing in spray application and rapid curing properties. The sulfur-neoprene may be accelerated strongly by means previously described, for self-curing at room temperature, a property which is important for manufacturing plants which are not equipped with curing ovens. This type of neoprene and a method for its preparation are fully described in U. S. Patent 2,351,735. In this product, the sulfur is in chemical combination with the polychloroprene and is made by polymerizing chloroprene (2-chloro-1,3 butadiene) in the presence of elementary sulfur. Other types of neoprene are not particularly adapted for use in the present invention.

The compositions of this invention are importantly useful as temporary protective coatings against weathering and corrosion in all climates, including also excellent resistance to salt water, abrasion and scuffing during shipping and storage for many articles for use in the present war such as aircraft, guns and replacement parts for all types of mechanical equipment which are shipped to all parts of the world and which must be received in perfect condition for effective use. Post-war utilities are exemplified by the use of these compositions on such units as refrigerators, washing machines, farm equipment, tractors, hydraulic presses, outboard motors and many other types of household and industrial equipment particularly when manufactured for export shipment. Many such items are finished in the factory with a conventional permanent protective and decorative coating in which the essential film-forming component is a synthetic resin (for example, a modified alkyd resin) or a drying oil (orthodox oleo-resinous varnishes) and in such instances, the improved strippable coatings are likewise useful as temporary coatings, since they insure the customer's receiving the article in an un-marred condition.

The present invention affords numerous unique advantages. Of particular importance is the critical and exact balance of the degree of adhesion to metal surfaces, including polished steel and aluminum alloys, which permits ready stripping of the film by hand but which is such that the film is not loosened or inadvertently stripped away by wind, exposure to water or ordinary mechanical abrasion and scuffing normally encountered during handling in shipping and storage. A peculiar advantage resides in the retention of strippability over extended periods after application of the coating, without any tendency to develop increased adhesion such as is apparent in many other types of strippable coatings. The new coatings afford outstanding resistance to corrosion on the metal surface substrate under the most severe climatic conditions and on exposure to salt water. The compositions of this invention

provide coatings which are tough, resilient, and flexible even at low temperature extremes. The coatings possess in high degree the property of reflecting light and heat thus contributing importantly to durability on outdoor exposures. They are also resistant to volatile aliphatic hydrocarbons, oils and greases and have unusually low permeability to the passage of water vapor, a property which enhances their ability to withstand corrosion conditions. The compositions may also be applied by spraying, thus extending their utility for coating larger units where dipping or other means of application is impractical.

It is apparent that many widely different embodiments of the invention may be made without departing from the spirit and scope thereof; and, therefore, it is not intended to be limited except as indicated in the appended claims.

I claim:

1. A corrosion-resistant, sprayable, strippable coating composition comprising, by weight, 100 parts of an uncured chloroprene polymer obtained by polymerizing chloroprene in the presence of an amount of elementary sulfur up to 2% by weight of the chloroprene, a curing accelerator for the said chloroprene, 15-50 parts of finely divided aluminum powder, and a liquid volatile vehicle containing a solvent for the chloroprene.

2. A corrosion-resistant, sprayable, strippable coating composition comprising, by weight, 100 parts of an uncured chloroprene polymer obtained by polymerizing chloroprene in the presence of an amount of elementary sulfur up to 2% by weight of the chloroprene, a curing accelerator for the said chloroprene, about 15-50 parts of finely divided aluminum powder, about 0.05-5.0 parts of an auxiliary stripping agent selected from the group consisting of soya lecithin, a lead soap of petroleum oil acids, and a stearyl alcohol ester of a styrene-maleic anhydride reaction product, and a liquid volatile vehicle containing a solvent for the chloroprene.

3. The composition of claim 2, in which the aluminum powder is present in an amount of about 40 parts by weight.

4. The composition of claim 2 in which the auxiliary stripping agent is soya lecithin.

5. The composition of claim 2 in which the auxiliary stripping agent is a lead soap of petroleum oil acids.

6. The composition of claim 2 in which the auxiliary stripping agent is a stearyl alcohol ester of a styrene-maleic anhydride reaction product.

7. A corrosion-resistant, sprayable, strippable coating composition comprising, by weight, 100 parts of an uncured chloroprene polymer obtained by polymerizing chloroprene in the presence of an amount of elementary sulfur up to 2% by weight of the chloroprene, about 15-50 parts of finely divided aluminum powder, about

0.05-5.0 parts of an auxiliary stripping agent selected from the group consisting of soya lecithin, a lead soap of petroleum oil acids, and a stearyl alcohol ester of a styrene-maleic anhydride reaction product, about 2-8 parts of a butyraldehyde monobutylamine condensation product, about 18-72 parts of a 47.6% litharge slurry in xylene, and a liquid volatile vehicle containing a solvent for the chloroprene.

8. The composition of claim 7 in which the aluminum powder is present in an amount of about 40 parts by weight and the auxiliary stripping agent is soya lecithin and is present in an amount of about 2 parts by weight.

9. A corrosion-resistant, sprayable, strippable coating composition of approximately the following composition:

	Percent by weight
Uncured chloroprene polymer obtained by polymerizing chloroprene in the presence of an amount of elementary sulfur up to 2% by weight of the chloroprene.	17.80
Piperidinium pentamethylene dithiocarbamate	0.21
Phenyl-β-naphthylamine (antioxidant)	0.36
Stearic acid	0.36
Calcined magnesias (extra light)	0.72
Zinc oxide	0.18
Toluene	34.65
Xylene	34.60
Mineral spirits	3.72
Aluminum powder	7.40
	100.00

and a curing accelerator for the said chloroprene.

10. An article of manufacture comprising a corrodable metal substrate carrying a tough, corrosion-resistant, strippable coating comprising, by weight, 100 parts of an uncured chloroprene polymer obtained by polymerizing chloroprene in the presence of an amount of elementary sulfur up to 2% by weight of the chloroprene, a curing accelerator for the said chloroprene, and 15-50 parts of finely divided aluminum powder, the thickness of the dry film on the metal substrate surface being between about 4 and 9 mils.

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