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3,063,873

DECONTAMINATION PROCESS UTILIZING ALKALI-SENSITIVE COATINGS

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No Drawing. Filed Feb. 8, 1960, Ser. No. 7,494
5 Claims. (Cl. 134-4)

(Granted under Title 35, U.S. Code (1952), sec. 266)

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

The present invention relates to a decontamination process and, more particularly, to one employing either alkali-solution-removable or hot-water-removable protective coatings.

The protection of surfaces from contaminants has been a continual problem which has received an upsurge of attention with the advent of atomic weapons and the resulting danger from radioactive particles. In addition to the more notorious radioactive fallout contamination, contaminating substances such as dirt, grit, tar, paint, grease, oil, organic debris, concrete, living organisms and metal particles have long posed a problem. Most attempts at removing these contaminants from surfaces have involved the use of detergents. In addition to the expense involved this often yields an unsatisfactory removal of these contaminants. Small particles of the contaminant, such as radioactive particles, for instance, settle into the pores of the paint covering the surface and are very difficult to "scrub" out. To accomplish complete removal of the contaminant sandblasting or some other equally difficult and expensive procedure then has been resorted to.

According to the present invention, the surface-to-be-protected is coated prior to exposure to contamination with a protective coating composition which forms upon the surface a dry film of high durability and high weathering capability. The nature of the coating composition employed is such that the resulting film has excellent wear and weathering properties and is at the same time hot-water-removable. After the coated surface has been exposed to contamination it is then subjected to hot water (fresh, brackish, or seawater) under pressure. The coating (dry film), now contaminated, under the action of the hot water or steam under pressure loses its adhesive capability and is stripped from the surface. As an application example, such a composition would be applied to the skin of a naval vessel to serve thereon as a durable protective coating. After nuclear attack this coating would be washed away by the steam or hot water carrying with it the radioactive particles embedded therein, thereby freeing the ship from contamination.

To meet situations where a severe degree of contamination is to be encountered the invention embraces the use of easily-removed undercoatings to supplement the aforementioned top protective coating. The undercoating serves as an additional barrier between the contaminants and the to-be-protected surface. As with the top protective coating, this undercoating is removed, after contamination, from the surface it covers and carries along with it any contaminants which have penetrated past the top coating. In one embodiment an alkali-removable undercoating is used. To illustrate use of the hot-water-removable top coating and an alkali-removable under-

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coating consider a ship at sea trapped in radioactive fallout. By subjecting the exposed surfaces of the ship with hot seawater under pressure somewhere from 90-95% of the radioactive particles are removed along with the hot-water-removable top coating in a process of "tactical decontamination." After the ship has returned to shipyard the alkali-sensitive undercoating along with the remaining contaminants is removed by the application of a mild alkali solution. In another embodiment a water-sensitive undercoating is employed. This water-sensitive undercoating may vary considerably in adhesive and cohesive properties from the top protective coating. This water-sensitive undercoating is removed, after contamination exposure, at the same time as the top coating under the action of the pressured hot water or steam and, in fact, usually expedites the removal of the top coating.

The invention further contemplates the use of an alkali-sensitive coating as the sole coating to be applied to the to-be-protected surfaces. Such a coating may be removed in whole or in part to meet various degrees of contamination.

An object of the present invention is to provide a quick, facile, and economical method for freeing surfaces from contaminants, including radioactive contaminants.

A further object is to provide a decontamination process which, as one of its steps, provides a normal, durable protective covering for surfaces involved.

Another object is to provide a decontamination process capable of freeing surfaces from a severe degree of contamination.

An additional object is to provide a coating composition which serves as a protective coating under normal operating conditions and which easily can be sloughed off after contamination to free the coated surface of contaminants.

A further object is to provide a protective coating composition whose dry film can be controllably and easily removed in whole or to a selected fraction of its original thickness.

Still another object is to provide a paint system of coatings and undercoatings which join to give protective coating to a surface under normal operating conditions and which can be sloughed off after exposure to severe contamination to leave the surface contamination-free.

Other objects and many of the attendant advantages of this invention readily will be appreciated by reference to the following detailed description.

The basic coating composition of the invention comprises essentially a high polymer plastic of either the elastomeric type or the thermoplastic type, or a combination of both, formulated with a water-sensitive adhesion modifier. The polymer plastic is substantially water-insoluble and may possess various degrees of cohesive or adhesive properties. The elastomeric type commonly possesses excellent cohesive properties and is limited to poor adhesive properties; the thermoplastic types possess a range of various degrees of cohesive and adhesive properties. This water-sensitive adhesion modifier must be of a type capable of at least maintaining the adhesive property of the particular plastic and, preferably, of increasing this adhesive property. The water sensitive adhesion modifier is preferably, but not necessarily, a film-forming material.

Among suitable high polymer elastomeric materials are

the natural and synthetic rubbers. Some of the synthetic rubbers are: styrene-butadiene co-polymers (Buna S or GR-5), the chlorobutadiene polymers (neoprene or GR-M), the butadiene-acrylonitrile polymers (Buna N or GR-N), iso-butylene copolymers (s-Polymers), butyl rubber or GR-I, polyisobutylene (Vistanex) and polysulfide rubbers (Thiokol).

Among suitable polymer thermoplastics are the following: the bitumens vinyls, polystyrene, polyethylene, acrylics and silicones. Among the vinyls are included: vinylidene chloride, polyvinyl butyral, vinyl chloride copolymers, polyvinyl chloride and polyvinyl acetate. Other appropriate thermoplastics include celluloses, such as ethyl cellulose, benzyl cellulose, cellulose acetate, cellulose acetate butyrate, and polyamides, alkyds and glyptals.

The water-sensitive adhesion modifier, sometimes hereinafter referred to as an "adhesion modifier" may include as a broad class a hydrophilic film-forming material which in waterborne systems embraces latices and water emulsions and which is known as a thickener or protective colloid. Usually this type of material promotes adhesion at ambient conditions and may further be described as a material which shows physical change in the manner of film deficiency when subjected to hot water up to 212° F. under pressure. Some typical examples of suitable water-sensitive adhesion modifiers are: polyamide 115 (General Mills: a reaction product of dimerized and trimerized linolenic and linolenic acids with ethylene diamine), hide glue, bone glue, gelatin, sodium alginate, gum arabic ammonium caseinate, sodium carboxymethyl cellulose, polyvinyl alcohol, methyl cellulose, sodium polyacrylate, polyethylene glycol, carbowax polyethylene glycol (Union Carbide and Carbon Company), Santicizer 9 (Monsanto: mixture of ortho and para toluene sulfonamides), benzoic acid, acetanilide, diethylene glycol stearate, sodium stearate, polyvinyl methyl ether, aryl and alkyl sulfonates, glyceryl esters such as glyceryl monostearate and glyceryl mono laurate, glycol fatty acid esters such as ethylene glycol mono laurate and diethylene glycol stearate, polyethylene glycol fatty acid esters such as carbowax 4000 mono laurate and polyethylene glycol distearate and other hydrophilic materials commonly classed as wetting agents or emulsifiers such as fatty acid amines or derivatives and alkali fatty acid soaps. Although not typically film formers, certain alkali materials, such as sodium or potassium hydroxide, have also been utilized. The preferred type of water-sensitive adhesion modifier is the film-forming type although the non-film-forming types can be utilized under certain non-critical conditions.

The sought-for goal in the formulation of the high polymer plastic with the water-sensitive adhesion modifier is the production of a coating which is sufficiently cohesive and adhesive to provide adequate protective covering and which at the same time is easily removed by the application of hot water or steam under pressure. When a high polymer plastic possessing poor or limited adhesion, and unmodified, is applied as ordinary paint over typical surfaces, such as metal surfaces, painted or unpainted, glass, wood, concrete, asphalt, rubber, etc., it will show loss of adhesion in a relatively short time as evidenced by peeling. Commonly, when increments of water-sensitive adhesion modifiers are added to such a plastic of low adhesive properties, the adhesion characteristic of the resulting composition increases, each addition of adhesion modifier promoting up to a point the adhesive properties of the dry film of the composition. Generally, as the value of adhesion is increased, the value of cohesion decreases. The value of cohesion, however, does not decrease to the point that an unsatisfactory film will result. Thus, the addition of water sensitive adhesion modifier to the high polymer plastic produces a composition wherein adhesion is improved and the film therefrom still retains good cohesive characteristics.

In the method employed herein the above-described composition is applied to the surface, which, it is anticipated, may later be subjected to contamination, and on drying becomes a durable protective coating capable of withstanding typical weathering. Even though the coating may exhibit some leaching effect during atmospheric exposure because of the water-sensitive adhesion modifier, this action is slow and the net durability of the coating is retained for extended periods of months. After the coated surface has been subjected to contamination hot water or steam under pressure is applied to the dry film of the composition. The adhesion modifier reacts to the hot water or steam to become mobile by dissolving, dispersing, or swelling, simultaneously lowering the adhesion of the entire film. Then the impact of the water or steam under pressure ruptures the film and separates the coating from the surface with subsequent complete removal of the coating and the contaminants it contains. The rate of removal of the film is proportional to the rapidity with which the adhesion modifier employed is dissolved, swollen, or dispersed by the pressured hot water or steam.

When reference is made to the make-up of the coating composition it is to be understood that the constituents of the dry film are of primary significance. On the other hand, the composition of the wet film may vary, particularly in relation to the addition of solvents to render the composition applicable to the purpose at hand. It is obvious that, if a solvent paint is too thick to apply, adding some solvent will render it more applicable; the composition of the dry film will not have been altered thereby.

It is obvious to one skilled in the art that certain modifications in composition can be made to produce a given coating composition in three different forms or types: namely as a hot melt, solvent system, or waterborne system. Examples are:

		Parts by weight	
		Example 1	Example 2
(1) HOT MELT SYSTEM			
40	Ethyl cellulose N-14 (Hercules).....	70	30
	Polyamide 115 (General Mills).....	30	70
	(A-5 stabilizer) (carbide chemicals-epoxy stabilizer).....	(1)	(1)
	(Doenax, antioxidant) (may be added to prevent discoloring).....	(1)	(1)
(2) SOLVENT SYSTEM			
50	Dry film:		
	Ethyl cellulose (N-14).....	70	30
	Polyamide 115.....	30	70
	Wet film:		
55	Ethyl cellulose sol. 15% in xylene.....	466	200
	Polyamide 115, 20% in xylene.....	150	350
(3) WATERBORNE SYSTEM			
60	Ethyl cellulose N-14.....	70	30
	Polyamide 115.....	30	70
	Ammonium caseinate, 15% sol.....	18-36	18-36
	Triethanolamine oleate.....	3-9	3-9
	Water.....	200-400	200-400

The above listed formulations based on equal dry film thickness should produce reasonably similar films of a representative composition.

Application techniques may vary from one formulation to another. For example, the hot melt formulation of Example 2 is viscous and best can be applied by troweling or by using high-pressure spray equipment. However, if the amount of ethyl cellulose is reduced and replaced by more water-sensitive adhesion modifier, as shown by Example 3, the viscosity is lowered and application of the coating composition can be done easily with conventional hot melt equipment.

Some other examples of the hot melt type of coating composition of the invention are as follows with some physical properties included:

5 HOT MELT FORMULATIONS

	Example 7	Example 8	Example 9
Ethyl cellulose N-14.....	50.....	33.....	33.
Santicizer 9.....	50.....	66.....	33.
Castor wax (polymerized castor oil-Baker's).....	-----	-----	33.
Stearic acid.....	-----	-----	-----
Polyamide 115.....	-----	-----	-----
Film.....	Some flexibility.	Hard.....	Flexible.
Viscosity.....	Very viscous.	Lower than (1).	Lower than (2).
Application.....	Trowel with difficulty.	Can trowel.....	Spray with difficulty.
Adhesion.....	Fairly good.....	Fair.....	Fair.
	Example 10	Example 11	Example 12
Ethyl cellulose N-14.....	25.....	50.....	33.
Santicizer 9.....	25.....	-----	-----
Castor wax (polymerized castor oil-Baker's).....	25.....	-----	-----
Stearic acid.....	25.....	-----	-----
Polyamide 115.....	-----	50.....	66.
Film.....	Flexible.	Some flexibility.	Hard.
Viscosity.....	Lowest.....	Very viscous.	Lower than (1).
Application.....	Can spray.....	Trowel with difficulty.	Can trowel.
Adhesion.....	Fair.....	Fairly good.....	Fair.

It is obvious that all of the above melt coating compositions also can be formulated as solvent systems or water-borne systems as known to the art and as illustrated by Examples 1 through 6.

The following compositions were tested by being applied over previously painted metal panels and the properties of adhesion and cohesion of the resulting films observed after six weeks of outdoor exposure:

Table 1

	Example 13	Example 14	Example 15
Formula—Dry film:			
Ethyl cellulose, N-14.....	100.....	90.....	80.
Santicizer 9.....	0.....	10.....	20.
Formula—Wet film:			
Ethyl cellulose sol. 15% in xylene.....	666.....	600.....	533.
Santicizer 9 sol. 20% in Cellosolve.....	0.....	50.....	100.
Exposure results:			
Adhesion.....	Poor.....	Poor.....	Fair.
Cohesion.....	Excellent.....	Excellent.....	Very good.
Dry film.....	Tough.....	Tough.....	A little flexible.
Condition.....	Peeling.....	Peeling.....	Some peeling.
Approximate pounds of pull required to strip a 1" pulling piece.....	Less than 1.....	Less than 1.....	About 1.
	Example 16	Example 17	Example 18
Formula—Dry film:			
Ethyl cellulose, N-14.....	70.....	60.....	50.
Santicizer 9.....	50.....	40.....	50.
Formula—Wet film:			
Ethyl cellulose sol. 15% in xylene.....	466.....	400.....	333.
Santicizer 9 sol. 20% in Cellosolve.....	150.....	200.....	250.
Exposure results:			
Adhesion.....	Good.....	Very good.....	Excellent.
Cohesion.....	do.....	Fairly good.....	Fair.
Dry film.....	Flexible.....	Flexible.....	Hard.
Condition.....	No peeling.....	No peeling.....	No peeling.
Approximate pounds of pull required to strip a 1" pulling piece.....	About 3-5.....	About 3-5.....	About 5-6.

From the results of the above exposure test, it can clearly be seen that Examples 13, 14 and 15 would be unsatisfactory as coating composition of the invention for long periods of outdoor exposure because of the loss of adhesion and the subsequent peeling of the dry film at ambient temperatures and conditions. Hence Examples 16, 17 and 18 would be more practical and useful when long periods of exposure are anticipated.

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It is obvious that the coating composition of the invention should adhere permanently to the surface to which it is applied until such time as the contaminant has been planted and removal of the contaminant is desired.

As previously stated, this invention relates to the decontamination of surfaces by the complete removal of a previously-applied protective coating by playing hot water or steam, under pressure, over said surfaces. Accordingly, the "removal rate" is an important characteristic of the given composition. To test the removal rates of given compositions an automatic traveling device housing a specially arranged jet of hot water at a predetermined temperature and pressure, at a given angle of impact, and at a predetermined distance from panels coated with the individual compositions was sped past each part at a given uniform speed. Removal tests conducted on panels coated with compositions of Examples 17 and 18 after 6 weeks of outdoor exposure, for example, showed the following results (removal of the coating is noted in square inches per pass):

Table 2

	Example 17		Example 18	
Water pressure (lbs./sq. in.).....	100	185	100	185
Water temperature (° F.).....	170	170	170	170
Sq. inches removal per pass.....	2	10	0	1

The results of this particular test indicate that Example 17 coating composition was more readily removed than Example 18 coating composition. Hence, if the requirements were such in this particular series of coating compositions that fast removal were required, Example 16 or 17 coating compositions would be used in preference to Example 18 coating composition.

Using adhesion modifiers other than Santicizer 9 faster removal rates were obtained as indicated by the following removal test results. (Formulas are all by parts by weight.)

Table 3

		Example 19	Example 20	Example 21			
45	Formula—Dry film:						
	Benzoic acid.....	50		30			
	Acetanilide.....		50				
	Ethyl cellulose, N-14.....	50	50	70			
	Polyamide 115.....						
50	Formula—Wet film:						
	Benzoic acid sol. 20% in Cellosolve.....	250		150			
	Acetanilide sol. 20% in Cellosolve.....		250				
	Ethyl cellulose N-14 sol. 15% in xylene.....	333	333	466			
	Polyamide 115, 20% in xylene.....						
	Removal tests—Formula:						
55	Water pressure (lbs./sq. in.).....	35	100	35	100		
	Water temperature (° F.).....	140	140	140	140		
	Sq. inches removed per pass.....	24	50	12	35	15	45

		Example 22	Example 23	
60	Formula—Dry film:			
	Benzoic acid.....			
	Acetanilide.....	30		
	Ethyl cellulose, N-14.....	70	60	
	Polyamide 115.....		40	
65	Formula—Wet film:			
	Benzoic acid sol. in 20% Cellosolve.....			
	Acetanilide sol. 20% in Cellosolve.....	150		
	Ethyl cellulose N-14 Sol. 15% in xylene.....	466	400	
	Polyamide 115, 20% in xylene.....		200	
	Removal tests—Formula:			
	Water pressure (lbs./sq. in.).....	35	100	100
	Water temperature (° F.).....	140	140	140
70	Sq. inches removed per pass.....	30	40	80

It can clearly be seen that the removal rates of the dry film of the coating composition shown in Table 3 are greater than the removal rates for the type of formulas shown in Table 1.

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By varying the water sensitive adhesion modifier as to the hot water sensitivity property, various rates of removal can be effected. The following coating compositions of the invention given in Table 4 showed in general very fast removal rates.

Table 4

	Examples						
	24	25	26	27	28	29	30
Formula—Dry film: Ethyl cellulose, N-14 (Hercules).....	80	70	60	50	40	30	20
Polyamide 115 (General Mills).....	20	30	40	50	60	70	80
Formula—Wet film: Ethyl cellulose, N-14 15% sol. in xylene.....	533	466	400	333	266	200	133
Polyamide 115 20% sol. in xylene.....	100	150	200	250	300	350	400

It has been found that the removal rate is sufficiently rapid to be practical only if a minimum of 10% by weight of water-sensitive adhesion modifier is used, this 10% being figured on the total weight of the film-forming constituents of the dry film of this composition.

There also appears to be a lower limit to the quantity of high polymer plastic required for a satisfactory composition, this amount being about 10% of the total weight of the film-forming constituents of the dry film of the composition.

The invention contemplates the use of supplementary materials in addition to the high polymer plastic and the water-sensitive adhesion modifier. These supplementary materials usually are economical and their use in combination with the high polymer plastic and the adhesion modifier would greatly reduce costs and yet not seriously alter the required film characteristics of adhesion and cohesion. Such supplementary materials usually are water-insoluble and comprise natural and synthetic resin, vegetable, mineral and petroleum wax, synthetic wax, metallic soap, plasticizer or fatty acid. Said supplementary materials may perform certain functions such as, for example, reducing the viscosity of a hot melt composition. As a specific example, the stearic acid and castor wax of Example 10 greatly reduce the viscosity of the molten coating composition thus permitting ease of application. The amount of supplementary materials used can be varied up to about 60% by weight based on the film forming constituents of the dry film of the coating composition. The basic composition may be loaded with a variety of pigments.

The following are further representative examples of the invention along with the mixing processes involved:

HOT MELT

Example 31

Santicizer 9 (Monsanto)	25
Stearic acid	25
Glyceryl monostearate (Aldo 33 Glyco Co.)	25
Ethyl cellulose (N-14, Hercules)	25

Process.—Heat Santicizer 9, stearic acid and glyceryl monostearate together and gain 280° F.. Slowly with agitation sprinkle in ethyl cellulose. Continue to agitate until ethyl cellulose is dispersed and gain 300° F. and off fire.

	Example 32	
	(A)	(B)
Ethyl cellulose, N-14.....	60.....	20.
Polyamide 115.....	40.....	80.
Antioxidant and heat stabilizer may be added 1% by weight Deenax and A-5.	Very viscous.	Fluid.

Process.—Heat Polyamide to about 275° F. Sprinkle

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in ethyl cellulose and agitate until dispersed. Gain 300° F. and off fire.

	Example 33	
	(A)	(B)
Ethyl cellulose, N-14.....	60.....	20.
Polyvinyl methyl ether.....	40.....	80.
Antioxidant and heat stabilizer may be added 1% by weight Deenax and A-5.	Very viscous.	Fluid.

Process.—Heat polyvinyl ether to 275° F. Sprinkle in ethyl cellulose and agitate until dispersed. Gain 300° F. and off fire.

Example 34

Santicizer 9	66
Polyvinyl acetate	33

Process.—Heat Santicizer 9 to melt. At 280° F. add polyvinyl acetate. Continue agitation until dispersed. When uniform, take off fire. Do not exceed 350° F.

	Example 35				
	A	B	C	D	E
Santicizer 9.....	40	33	25	33.3	22.2
Glyceryl monostearate.....	40	33	25	22.2	33.3
Castor wax (Baker's polymerized castor oil).....	20	33	25	22.2	22.2
Ethyl cellulose N-14.....	20	33	25	22.2	22.2

Process.—Heat to melt all ingredients except ethyl cellulose. Gain 280° F. Then with agitation slowly sprinkle in ethyl cellulose. Continue agitation until ethyl cellulose is uniformly dispersed. Gain 300° F. and off fire.

Example 36

Glyceryl monostearate	25
Santicizer 9	25
Castor wax	25
Polyisobutylene (Vistanex LM-MS, Enjay Co.)	25

Process.—Heat glyceryl monostearate, Santicizer 9 and castor wax to around 250° F. Add Vistanex LM-MS and with agitation disperse Vistanex. When uniform, gain 300° F. and off fire.

SOLVENT SYSTEMS

	Example 37					
	A	B	C	D	E	F
Glyceryl monostearate.....	10	10	10	10	10	10
(Vistanex B-100 solids).....	(4.4)	(5.3)	(8.8)	(9.7)	(13.2)	(17.6)
Vistanex B-100, 8.8% sol. in mineral spirits.....	50	60	100	110	150	200
Mineral spirits.....	40	40	40	40	40	40
Magnesium silicate.....	12	12	16	16	20	24
Titanium calcium.....	6	6	8	8	10	12

Process.—Heat glyceryl monostearate to melt. At 250° F. slowly add Vistanex B-100 solution. Then add mineral spirits. Then add magnesium silicate and titanium calcium and grind or run through colloid mill.

	Example 38						
	A	B	C	D	E	F	G
Dry film: Glyceryl monostearate (Aldo 33—Glyco Co.).....	30	40	50	60	35	45	55
Ethyl cellulose (N-14 Hercules).....	70	60	50	40	65	55	45
Wet film: Glyceryl 1 monostearate, 20% dispersion in naphtha.....	150	200	250	300	175	255	275
Ethyl cellulose, 15% solution in naphtha.....	466	400	333	266	433	366	300

Process.—Heat glyceryl monostearate to melt. Add naphtha, stir until cool. Grind. Dissolve ethyl cellulose in naphtha. Stir the glyceryl monostearate dispersion into the ethyl cellulose solution.

	Example 39						
	A	B	C	D	E	F	G
Dry film:							
Ethyl cellulose (N-14).....	80	70	60	50	40	30	20
Polyvinyl methyl ether.....	20	30	40	50	60	70	80
Wet film:							
Ethyl cellulose (N-14) 15% in xylene.....	533	466	400	333	266	200	133
Polyvinyl methyl ether 20% in toluene.....	100	150	200	250	300	350	400

Process.—Dissolve ethyl cellulose in xylene. Dissolve polyvinyl methyl ether in toluene. Add the ethyl cellulose solution to the polyvinyl methyl ether solution. (Note: A is too thick. Requires more solvent.)

	Example 40						
	A	B	C	D	E	F	G
Dry film:							
Vinylite VAGH (Bakelite vinyl resin with high percentage acetate).....	80	70	60	50	40	30	20
Polyamide 115.....	20	30	40	50	60	70	80
Wet film:							
Vinylite VAGH (Bakelite) (15% in methyl isobutyl ketone).....	533	466	400	333	266	200	133
Polyamide 115 (General Mills) (20% in Toluene).....	100	150	200	250	300	350	400

Process.—Dissolve vinylite in methyl isobutyl ketone. Dissolve polyamide in toluene. Add the polyamide solution to the vinylite solution slowly with constant stirring.

	Example 41						
	A	B	C	D	E	F	G
Dry film:							
Polyvinyl acetate AYAT.....	80	70	60	50	40	30	20
Santicizer 9.....	20	30	40	50	60	70	80
Wet film:							
15% polyvinyl acetate AYAT in isopropyl, 90% by weight; water, 10% by weight.....	533	466	400	333	266	200	133
20% Santicizer 9 in Cellosolve.....	100	150	200	250	300	350	400

Process.—Dissolve polyvinyl acetate in a mixture of 90% isopropyl alcohol and 10% water. Dissolve Santicizer 9 in Cellosolve. Mix the two solutions.

	Example 42						
	A	B	C	D	E	F	G
Dry film:							
Polyvinyl acetate (AYAT).....	80	70	60	50	40	30	20
Polyamide 115.....	20	30	40	50	60	70	80
Wet film:							
15% sol. polyvinyl acetate AYAT in ethyl alcohol-water (25:1).....	533	466	400	333	266	200	133
20% polyamide 115 in toluene.....	100	150	200	250	300	350	400

Process.—Dissolve polyvinyl acetate in ethyl alcohol-water mix (25:1). Dissolve polyamide 115 in toluene. Stir the two solutions together.

WATERBORNE SYSTEMS

	Exempl 43				
	A	B	C	D	E
5					
10					
15					
20					
25					
30					
35					
40					
45					
50					
55					
60					
65					
70					
75					

	Exempl 43				
	A	B	C	D	E
FORMULA					
Dry film:					
A. High polymer plastic:					
1. Rhoplex AC-33, solids (Rohm & Haas, polyacrylate water emulsion).....	80	90	80	90	---
2. Bks. 114, solids (Bakelite polystyrene water emulsion).....	---	---	---	---	80
3. WC-130, solids (Bakelite, polyvinyl acetate emulsion).....	---	---	---	---	---
B. Water sensitive adhesion modifier:					
4. Hide glue.....	20	10	---	---	---
5. Sodium carboxymethyl cellulose.....	---	---	20	10	---
6. Polyvinyl methyl ether.....	---	---	---	---	20
7. Gum arabic.....	---	---	---	---	---
Wet film:					
Rhoplex, AC-33, 46%.....	174	195	174	195	---
Bks. 114, 40%.....	---	---	---	---	200
WC-130, 60%.....	---	---	---	---	---
Hide glue, 2 1/2% aqueous.....	800	400	---	---	---
NaCMC, 2 1/2% aqueous.....	---	---	800	400	---
Polyvinyl methyl ether 20% aqueous.....	---	---	---	---	100
Gum arabic, 50% aqueous.....	---	---	---	---	---
FORMULA					
Dry film:					
A. High polymer plastic:					
1. Rhoplex AC-33, solids (Rohm & Haas, polyacrylate water emulsion).....	---	80	90	---	---
2. Bks. 114, solids (Bakelite polystyrene water emulsion).....	90	---	---	---	---
3. WC-130, solids (Bakelite, polyvinyl acetate emulsion).....	---	---	---	80	90
B. Water sensitive adhesion modifier:					
4. Hide glue.....	---	---	---	---	---
5. Sodium carboxymethyl cellulose.....	---	---	---	20	10
6. Polyvinyl methyl ether.....	10	---	---	---	---
7. Gum arabic.....	---	20	10	---	---
Wet film:					
Rhoplex, AC-33, 46%.....	---	174	195	---	---
Bks. 114, 40%.....	225	---	---	---	---
WC-130, 60%.....	---	---	---	133	150
NaCMC, 2 1/2% aqueous.....	---	---	---	---	---
Polyvinyl methyl ether 20% aqueous.....	60	---	---	100	60
Gum arabic, 50% aqueous.....	---	40	20	---	---
FORMULA					
Dry film:					
a. Latex Bks. 114, 40% (Bakelite's) polystyrene emulsion, solids.....	20-80	---	---	---	---
b. Latex Rhoplex AC-33 46% (Rohm & Haas) emulsion polyacrylate, solids.....	---	---	---	20-80	---
c. Adhesion modifier emulsion, 30% solids Santicizer 9 ¹ (Monsanto), solids.....	80-20	---	---	80-20	---
Wet film:					
a. Latex Bks. 114, 40%.....	50-200	---	---	---	---
b. Latex Rhoplex AC-33, 46%.....	---	---	---	44-170	---
c. Santicizer 9 ¹ emulsion 30%.....	266-66	---	---	266-66	---
1 Santicizer 9 Emulsion 30% (mixture of ortho and para toluene sulfonamides).					
Process.—Stir the emulsion together, avoiding excessive beating of air into the mix.					
SANTICIZER 9 EMULSION					
Santicizer 9.....	100				
15% aqueous sol.—Ammonium caseinate.....	36				
Triethanolamine oleate.....	6				
(1) Water.....	44				
(2) Water.....	200				
Process. Heat Santicizer 9 and (2) 200 parts of water to boiling. Add the mixture of ammonium caseinate, triethanolamine oleate and (1) 44 parts water. Stir vigorously. Grind or run through homogenizer.					
Example 45					
Resin base:					
Santicizer 9 (Monsanto).....	65.5				
Stearic acid.....	65.5				
Glyceryl monostearate (Aldo 33, Glyco Co.).....	65.5				
Ethyl cellulose (N-14, Hercules).....	65.5				
	262.0				

Emulsion:

Resin base	262
15% aqueous sol. ammonium caseinate.....	90
Triethanolamine oleate	8
(1) H ₂ O	44
(2) H ₂ O*	1,000
ASP 100 filler, 64% aqueous slurry.....	155

* Add more water for application if required.

Process.—Resin base to 250° F. Add slowly to mix in Waring Blender of ammonium caseinate, triethanolamine oleate and (1) 44 water. Add ASP 100 slurry and water.

Example 46

Resin base:	
Glyceryl monostearate (Aldo 33)	65.5
Santicizer 9	65.5
Ethyl cellulose, N-14	131.0

Emulsion:

Resin base	262
Cellosolve (ethylene glycol monoethyl ether) ..	26
15% aqueous solution ammonium caseinate.....	45
Triethanolamine oleate	8
(1) Water	44
(2) Water	1344
Titanium calcium pigment	100
Magnesium silicate extender	200

Process.—Resin base to 250° F. Add Cellosolve. Then add mix slowly to mix in Waring Blender of ammonium caseinate, triethanolamine oleate, and (1) 44 water. Add titanium calcium and magnesium silicate alternately with remainder of water. Grind or run through homogenizer.

FORMULA	Example 47						
	A	B	C	D	E	F	G
Dry film:							
Lacquer-phase polyvinyl acetate emulsion, solids.....	80	70	60	50	40	30	20
Polyvinyl methyl ether.....	20	30	40	50	60	70	80
Wet film:							
Lacquer-phase polyvinyl acetate emulsion ¹ (46% solids).....	174	152	130	108	86	64	42
20% aqueous sol. polyvinyl methyl ether.....	100	150	200	250	300	350	400

¹ Lacquer-phase polyvinyl acetate (AYAA) emulsion:

(A) 82% lacquer phase:	
Polyvinyl acetate AYAA.....	50.0
Tricresylphosphate.....	5.0
Toluene.....	43.5
Oleic acid.....	1.5
	100.0

(B) 18% water phase:	
Distilled water.....	92.0
28% ammonium hydroxide.....	8.0
	100.0

Process.—Prepare phase A and B separately. To 18 parts by weight of water phase B add with stirring 82 parts by weight of lacquer phase A. If both phases are warmed emulsification takes place easier. Mix the lacquer-phase emulsion and the aqueous polyvinyl methyl ether solution.

Where an excessive degree of contamination is to be encountered, removable undercoatings are used to supplement the composition described above. This undercoating may be alkali-sensitive or, like the topcoating, also be water-sensitive. In the first instance, after the water-sensitive top-coating has been removed by the application of pressured hot water or steam, a mild alkali solution, such as soapy water or hot weak sodium hydroxide solution, is applied to remove the undercoating along with the balance of contaminants not carried off by the previously-removed top-coating film. In the second instance the topcoating and undercoating are removed together at the

pressured hot water or steam application. When the water-sensitive undercoating is used a dual removal action results. The removability of the water-sensitive topcoating is accelerated by the fast loss of adhesion caused by the water-sensitive undercoating giving way. Typical of water-sensitive materials which may be used in the undercoating are methyl cellulose, sodium alginate, and polyvinyl methyl ether. The alkali-sensitive coating may employ certain carboxylated polyvinyl acetate polymers such as Shawinigan's C3V10M or others of this series. A typical formulation for one such alkali-sensitive undercoating is as follows:

Example 48

	Parts by weight
C3V10M polymer (Shawinigan)	90
Butanol	105
Xylol	105

For some applications a mild alkali-soluble coating composition may be used as the sole coating applied over the surface to be protected. If such a coating is sufficiently thick (several thousandths of an inch for example) mono-molecular layers of the dry film may be removed by adjusting the alkali concentration of the solution used to wash away the contaminated portions of the dry film. In this manner all of the coating need not be removed at one time; removal of only that portion necessary to eliminate the contamination can thus be effectuated. Portraitive of suitable formulations for this sole alkali-removable coating composition are the following:

Example 49

	Parts by weight
Water base formulation (clear):	
C3V10M polymer resin (Shawinigan)	100
28% NH ₄ OH	3
Water	230
Pine oil	3

Example 50

	Parts by weight
Water base formulation (clear):	
C3V10M polymer resin (Shawinigan)	100
28% NH ₄ OH	5
Water	228
Pine oil	3

Pigments may be added to Examples 49 and 50 to produce camouflage or decorative colors.

Various modifications falling within the scope of normal skill in the art obviously may be resorted to and are contemplated by this invention.

What is claimed is:

1. A process for protecting surfaces liable to be subjected to contamination which comprises applying to said surfaces, prior to exposure of the surfaces to contamination, a relatively substantial layer of an alkali-sensitive coating composition whose dry film is removable by an alkali solution in proportion to the degree of alkalinity of the removing solution and washing said alkali-sensitive coating, after exposure of said surfaces to contamination, with an alkali solution whose alkalinity is adjusted to remove the contaminated portion of the coating but leave on the surfaces the uncontaminated portion of the coating.

2. The process of claim 1 wherein the composition of said alkali-sensitive coating comprises, by weight, about 29.7% polymer resin, about 0.9% ammonium hydroxide, about 68.5% water, and about 0.9% pine oil.

3. The process of claim 1 wherein the composition of said alkali-sensitive coating comprises, by weight, about 29.7% polymer resin, about 1.5% ammonium hydroxide, about 67.9% water, and about 0.9% pine oil.

4. An alkali-sensitive protective coating composition whose dry film is removable by an alkali solution in proportion to the degree of alkalinity of the removing solution comprising, by weight, about 29.7% polymer

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resin, about 0.9% ammonium hydroxide, about 68.5% water and about 0.9% pine oil.

5. An alkali-sensitive protective coating composition whose dry film is removable by an alkali-solution in proportion to the degree of alkalinity of the removing solution comprising, by weight, about 29.7% polymer resin, about 1.5% ammonium hydroxide, about 67.9% water, and about 0.9% pine oil.

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