

US PATENT OFFICE

Published by AsbestosClaims.Law
asbestosclaims.law/library/15382/1

X-Copy Take

United States Patent Office 3,485,790 Patented Dec. 23, 1969

1

3,485,790

FILLED ESTER-CONTAINING POLYMERS

George H. Potter, St. Albans, and Clyde J. Whitworth, Jr., and Nathan L. Zutty, Charleston, W. Va., assignors to Union Carbide Corporation, a corporation of New York

No Drawing. Filed June 29, 1965, Ser. No. 468,155
Int. Cl. C08f 45/04, 29/28
U.S. Cl. 260—41
12 Claims

ABSTRACT OF THE DISCLOSURE

Improved filled polymers are obtained by heating a mixture of an ester-containing polymer, a finely divided inorganic filler containing chemically bound water and an acidic or basic catalyst for a period of time sufficient to effect reaction between the polymer and the filler.

The invention relates to a process for producing improved filled polymers and to the improved filled polymeric compositions that are produced thereby. In a particular aspect, the invention relates to a process which comprises heating a mixture of an ester-containing polymer, a filler, and a catalyst. In another aspect, the invention relates to the compositions that are produced by the process of the invention.

Ester-containing polymers such as ethylene-vinyl acetate copolymer or ethylene-ethyl acrylate copolymer can be improved in heat resistance, stiffness, and other properties by adding certain reactive fillers such as colloidal silica to the polymers. The present invention is based upon the discovery that properties of esteh-containing polymess that contain reactive fillers inn be further improved by empolying a catalyst when the filler is added to the polymer. Accordingly, the process of the invention comprises mixing an ester-containing rolymer, a reactive filler, and a catalyst, for a period of time and at a temperature sufficient to effect a reaction between said polymer and said filler, and recovering the filled polymeric composition produced thereby.

The improved, filled polymeric compositions of the invention have one or more of the following characteristics:

(a) Improved high temperature resistance,
(b) Improved water and organic solvent resistance,
(c) Improved electrical properties,
(d) Higher tensile strength, and the like.

The polymers that are employed in the invention are the ester-containing thermoplstic polymers wherein the ester group is in a side group that is bonded to a polymeric chain composed of carbon-to-carbon bonds. Among the useful ester-containing polymers are those that contain polymerized vinyl acetate. For example, vinyl acetate homopolymers and vinyl acetate copolymers with one or more comonomers that are polymerizable along with vinyl acetate are useful. Among the vinyl acetate polymers contemplated are vinyl acetate homopolymer, vinyl acetate-ethylene copolymer, vinyl chloride-vinyl acetate copolymer, vinyl chloride-vinyl acetate-vinyl alcohol copolymer, vinyl chloride-vinyl acetate-maleic anhydride copolymer, styrene-vinyl acetate copolymer, vinyl chloride-vinylidene chloride-vinyl acetate copolymer, vinyl acetate-acrylonitrile copolymer, and the like. Vinyl acetate polymers that deserve particular mention are vinyl acetate homopolymer, ethylene-vinyl acetate copolymer and vinyl chloride-vinyl acetate copolymer. Ethylene-vinyl acetate copolymers are preferred.

The ester-containing thermoplastic polymer can be a homopolymer or a copolymer of an acrylic or a methacrylic acid ester. Specific illustrative examples include ethylene-ethyl acrylate copolymers, ethylene-methyl methacrylate copolymer, ethyl acrylate-methyl acrylate-vinyl acetate copolymer, ethyl acrylate-acrylonitrile copolymer, 2-ethylhexyl acrylate-acrylonitrile-ethyl acrylate copolymer, ethyl acrylate-dimethyl maleate-acrylonitrile copolymer, ethyl acrylate-octyldecyl methacrylate-acrylonitrile copolymer, methyl methacrylate-styrene-acrylonitrile copolymer, ethyl acrylate-vinyl chloride-acrylonitrile copolymer, butyl acrylate-vinylidene chloride copolymer, 2-methoxyethyl acrylate-acrylonitrile copolymer, 2-butoxyethyl acrylate-acrylonitrile copolymer, and the like. Many other ester-containing polymers are useful. For instance, ethylene-butyl maleate copolymer, ethylene-butyl fumarate copolymer, and the like are useful in the invention.

The preferred thermoplastic ester-containing polymers are copolymers of ethylene and one or more of vinyl acetate, alkyl acrylates wherein preferably the alkyl has up to 18 carbon atoms, alkyl methacrylates wherein preferably the alkyl has up to 18 carbon atoms, and alkyl maleates or fumarates wherein preferably the alkyl has up to 18 carbon atoms. Normally the thermoplastic ester-containing polymer will contain at least about 5 weight percent of the ester-containing monomer (in polymerized form), and preferably at least 15 weight percent of the ester-containing monomer, percentages being based upon weight of polymer. The molecular weight of the ester-containing polymer is such that the polymer is normally solid at room temperature (i.e., about 23° C.). The molecular weights of many of the thermoplastic ester-containing polymers that are useful in the invention can be further characterized by Melt Index as determined by the procedure described in ASTM D-1238-57T. Many of the polymers will have Melt Index values in the range of from about 0.1 to about 400, and preferably from about 0.5 to about 100.

Many other polymers can be employed in conjunction with the thermoplastic ester-containing polymer. Specific illustrative examples include polyethylene, polypropylene, ethylene-propylene copolymer, poly(vinyl chloride), vinyl chloride-acrylonitrile copolymer, polyacrylonitrile, ethylene-acrylonitrile copolymer, polyamides such as nylon 6, nylon 6/6, and the like, polyethylene terephthalate and other polyesters, the polybydroxy ether produced by reacting equimolar proportions of 3-chloro-1,2-epoxypropane and the disodium salt of 2,2-bis(4-hydroxyphenyl)-propane, and the like.

The filler that is employed in the invention can be one or more of colloidal silica, certain clays, certain aluminas, asbestos, and the like.

The silica that is employed in the invention is a finely divided silica having a surface layer of hydroxyl groups. The commercially available silicas that are useful in the invention are known to the art as colloidal silicas. Such silicas are composed of particles that have their maximum dimension in the range of from about 0.001 micron to about 0.1 micron, and have a specific surface area of at least about 100 square meters per gram, and preferably at least about 150 square meters per gram. The specific surface area can be measured by nitrogen adsorption in accordance with the method described in the article "A New Method for Measuring Surface Areas of Finely Divided Materials and for Determining the Size of Particles" by P. H. Emmett, in the publication "Symposium On New Methods for Particle Size Determination in the Sub-Sieve Range," published by the American Society For Testing Materials, Mar. 4, 1941.

The individual silica particles, which have their greatest dimension in the range of from about 0.001 to about 0.1 micron, can be in the form of aggregates having a much larger dimension. These aggregates are broken down when the silica is mixed with the other materials to form the compositions of the invention. The surface layer of hydroxyl groups on the silica particles are chemically bound

A 13633

the silica. There is thus provided a monomolecular layer of silanol groups on the surface of the silica particles.

The preparation of finely divided silica having a surface layer of hydroxyl groups can be by various methods known to the art. For instance, any of the following three procedures can be used to produce the silica that is used in the invention:

(1) A silica aerogel may be formed by gelling silicic acid in an alcohol-water solution and then converting the gel to an aerogel. This may be carried out by replacing most of the water of the gel with alcohol, heating the gel in an autoclave above the critical temperature of alcohol so that there is no meniscus between the liquid and gas phases and venting the vapors. In this way the liquid phase is removed without subjecting the gelled structure to the compressive forces due to the surface tension of the liquid-gas interface. A pulverized light fluffy powder of silica particles may then be formed by pulverizing the dry aerogel.

(2) Colloidal silicas may be prepared by vaporizing silicon dioxide at high temperature or producing silicon-containing vapor by burning ethyl silicate or silicon tetrachloride and thereafter collecting the "silica fume."

(3) Still another technique of preparing colloidal silicas is to precipitate silica from aqueous solution in such form that it can be dried to give a fine powder.

Additional descriptions of the nature and production of finely divided silica having a surface layer of hydroxyl groups can be found in the laterature. One such source is "The Colloid Chemistry of Silica and Silicates" by Ralph K. Iler (published in 1955).

Certain clays are useful as fillers in the invention. The clays that are useful in the invention are the colloidal grades having a specific surface area of at least about 150 square meters per gram and which have an average particle size of less than 1 micron. As is well known in the art, the exact composition of clays vary depending upon their source, but they are normally hydrated silicates of aluminum, magnesium, or iron or mixtures thereof. The preferred clays are those that are predominantly hydrated magnesium aluminum silicates.

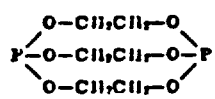
Hydrated aluminum oxide having a particle size such that the largest dimension is less than about 1 micron is useful as a filler in the invention.

Another filler that is useful in the invention is asbestos, preferably chrysotile asbestos.

The preferred filler for use in the invention is colloidal silica.

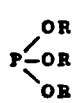
The discussion above points out that there are many different fillers that can be employed in the invention. The one feature that all of these fillers have in common, apart from small particle size, is that they are inorganic compositions that contain chemically bound water. Apparently, hydroxyl groups provided by the water react with the ester groups of the ester-containing polymer to thereby form a bond from the filler to the polymer. Chemically bound water is contrasted with moisture in that chemically bound water is not released until the filler is heated to a temperature above about 500°–600° C., while moisture is driven off at the boiling point of water.

The catalysts which have been found to promote the reaction between the filler and the thermoplastic ester-containing polymer are the non-neutral compositions, i.e., the acids and the bases. Any substance which is an acid or a base under either the Bronsted-Lowry theory (proton-transfer system) or the Lewis theory (electron-pair system) can be employed as a catalyst in the invention. Among the useful catalysts are found the phosphite esters, the titanate esters, certain organic tin compounds, proton acids (i.e., compounds that contain an acidic hydrogen atom), amines, alkali metal hydroxides and alkoxides, alkaline earth metal hydroxides and alkoxides, and many other classes of compounds that are either acids or bases. Specific illustrative phosphite esters include ethyl dihydrogen phosphite, decyl dihydrogen phosphite, phenyl dihydrogen phosphite, stearyl dihydrogen phosphite, diethyl hydrogen phosphite, di(2-ethylhexyl) hydrogen phosphite, diphenyl hydrogen phosphite, dibenzyl hydrogen phosphite, ditolyl hydrogen phosphite, dicyclohexyl hydrogen phosphite, trimethyl phosphite, triethyl phosphite, tripropyl phosphite, triisopropyl phosphite, tributyl phosphite, triisobutyl phosphite, tripentyl phosphite, triheptyl phosphite, trihexyl phosphite, trioctyl phosphite, trinonyl phosphite, tridecyl phosphite, triisodecyl phosphite, tridodecyl phosphite, trioctadecyl phosphite, tricyclohexyl phosphite, diethyl butyl phosphite, tribenzyl phosphite, triphenyl phosphite, tri-1-naphthyl phosphite tri-2-naphthyl phosphite, tri-1-anthryl phosphite, phenyl dimethyl phosphite, phenyl diethyl phosphite, phenyl dipropyl phosphite, phenyl dibutyl phosphite, phenyl dipentyl phosphite, phenyl diheptyl phosphite, phenyl dihexyl phosphite, phenyl dioctyl phosphite, phenyl dinonyl phosphite, phenyl didecyl phosphite, phenyl triisodecyl phosphite, phenyl didodecyl phosphite, 1-naphthyl didecyl phosphite, diphenyl methyl phosphite, diphenyl ethyl phosphite, diphenyl propyl phosphite, diphenyl butyl phosphite, diphenyl isobutyl phosphite, diphenyl pentyl phosphite, diphenyl heptyl phosphite, diphenyl hexyl phosphite, diphenyl octyl phosphite, diphenyl nonyl phosphite, diphenyl decyl phosphite, diphenyl isodecyl phosphite, diphenyl dodecyl phosphite, di-1-anthryl ethyl phosphite, triethylene diphosphite, i.e., the compound having the formula



tripropylene diphosphite, tributylene diphosphite, and the like. Many of the phosphites that can be employed in the invention can be represented by Formula I:

I



wherein each R individually can be hydrogen, alkyl, aryl, alkaryl, aralkyl, cycloalkyl, alkylene phosphite, and the like, provided that at least one R represents an organic group. Preferably, all three R groups represent organic groups. Normally, R will represent a group having not more than about 18 carbon atoms.

The catalyst can also be a titanate ester. Specific illustrative examples include tetramethyl titanate, tetraethyl titanate, tetraisopropyl titanate, tetrabutyl titanate, tetraoctyl titanate, tetra(2-ethyl-1,3-hexanediol) titanate, and other alkyl titanate esters wherein the alkyl groups have up to 18 carbon atoms.

Many organic tin compounds can be employed in the invention. Among the organic tin compounds that can be used are the stannous salts of alkanoic acids such as stannous octoate, stannous acetate, stannous laurate, stannous stearate, and the like. Also, the organotin compounds can be employed. Such compounds have at least one direct carbon-to-tin bond, and preferably, at least one bond to oxygen, sulfur, nitrogen, halogen, phosphorus, or hydrogen. Specific illustrative examples of useful organotin compounds include the following compositions:

(A) Tin compounds having four carbon to tin bonds such as tetramethyltin, tetraethyltin, tetrapropyltin, tetrabutyltin, tetraoctyltin, tetralauryltin, tetrabenzyltin, tetrakis(2-phenylethyl)tin, tetraphenyltin, tetraparatolyltin, tetravinyltin, tetraallyltin, tetrachloromethyltin, tetramethanesulfonylmethyltin, tetra-para-methoxy-phenyltin, tetra-paranitrophenyltin, as well as unsymmetrical compounds as exemplified by 2-cyanoethyl-tributyltin, dibutyldiphenyltin and various addition products of alkyl, aryl and aralkyltin hydrides with unsaturated organic com-

A 13634

pounds such as acrylonitrile, allyl cyanide, crotonitrile, acrylamide, methyl acrylate, allyl alcohol, acroleindiethyl acetal, vinyl acetate, styrene, and the like;

(B) Tin compounds having *n* carbon to tin bonds and 4-*n* bonds from tin to halogen or hydrogen atoms or hydroxyl groups in which *n* is an integer in the range of from 1 to 3, such as trimethyltin chloride, tributyltin chloride, trioctyltin chloride, triphenyltin chloride, trimethyltin bromide, tributyltin fluoride, triallyltin chloride, tributyltin hydride, triphenyltin hydride, trimethyltin hydroxide, tributyltin hydroxide, dimethyltin dichloride, dibutyltin dichloride, dioctyltin dicbloride, bis(2-phenylethyl)tin dichloride, diphenyltin dichloride, divinyltin dichloride, diallyltin dibromide, diallyltin diiodide, dibutyltin difluoride, bis(carboethoxymethyl)tin diiodide, bis(1,3-diketopentane)tin dichloride, dibutyltin dihydride, butyltin trichloride and octyltin trichloride;

(C) Tin compounds having two carbon to tin bonds and a double bond from tin to oxygen or sulfur, such as dimethyltin oxide, diethyltin oxide, dibutyltin oxide, dioctyltin oxide, dilaurylin oxide, diphenyltin oxide and diallyltin oxide, all prepared by hydrolysis of the corresponding dihalides, as well as bis-2-phenylethyltin oxide,

$$[HOOC(CH_2)_5]_2SnO$$

$$[CH_3OCH_2(CH_2OCH_2)_{x-1}CH_2]_2SnO$$

$$[CH_3OCH_2(CH_2OCH_2)_{x-1}CH_2O(CH_2)_5]_2SnO$$

and dibutyltin sulfide, the *x*'s being whole integers;

(D) Tin compounds having *n* carbon to tin bonds and 4-*n* bonds from tin to oxygen, sulfur, nitrogen or phosphorus linking organic radicals, *n* being an integer from 1 to 3, such as tributyltin methoxide, tributyltin butoxide, tributyltin acetate, tributyltin N-piperazinylthiocarbonylmercaptide, tributyltin phosphorus dibutoxide [prepared as indicated immediately below:

$$2(C_4H_9O)_3P + PCl_3 \longrightarrow 3(C_4H_9O)_2PCl$$

$$(C_4H_9)_3SnCl + 2Na \longrightarrow (C_4H_9)_3SnNa + NaCl$$

$$(C_4H_9)_3SnNa + (C_4H_9O)_2PCl \xrightarrow{NH_3} (C_4H_9)_3SnP(OC_4H_9)_2 + NaCl$$

dibutyltin dibutoxide,

$$(C_4H_9)_2Sn[OCH_2(CH_2OCH_2)_{x-1}CH_2CH_2]_2$$

dibutyl bis(O-acetylacetonyl)tin, dibutyltin bis(octyl maleate), dibutyltin bis(thiododecoxide), dibutyltin bis(octyl thioglycolate), dibutyltin bis(N-morpholinylcarbonylmethylmercaptide), dibutyltin dibenzenesulfonamine, dimethyltin diacetate, diethyltin diacetate, dibutyltin diacetate, dioctyltin diacetate, dilaurylin diacetate, dibutyltin dilaurate, dibutyltin maleate, dibutyltin bis(N-piperazinylthiocarbonylmercaptide), dioctyltin bis(N-piperazinylthiocarbonylmercaptide), octyltin tris(thiobutoxide), butyltin triacetate, methylstannonic acid, ethylstannonic acid, butylstannonic acid, octylstannonic acid,

$$HOOC(CH_2)_5\text{-}SnOOH,\ (CH_3)_3N(CH_2)_5SnOOH$$

$$CH_3OCH_2(CH_2OCH_2)_{x-1}CH_2SnOOH$$

and

$$CH_3OCH_2(CH_2OCH_2)_{x-1}CH_2O(CH_2)_5SnOOH$$

in which the *x*'s are positive integers.

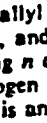
(E) Polystannic compounds having carbon to tin bonds and preferably also bonds from tin to halogen, hydrogen, oxygen, sulfur, nitrogen or phosphorus, such as

$$HOOSn(CH_2)_xSnOOH$$

and

$$HOOSnCH_2(CH_2OCH_2)_xCH_2SnOOH$$

the *x*'s being positive integers, bis-trimethyltin, bis-triphenyltin, bis-tributyl distannoxane, dibutyltin basic laurate, dibutyltin basic hexoxide and other polymeric organo-tin compounds containing carbon to tin bonds and preferably also bonds, e.g., those having repeating



groups, dimers and trimers of $(R_2SnY)_n$ and the like in which the R's may be alkyl, aryl or aralkyl radicals and the Y's are chalcogens, as well as many other organo-tin compounds heretofore proposed as heat and light stabilizers for chlorinated polymers and available commercially for this purpose.

The preferred tin compounds are the stannous alkanoates and the dialkyltin compounds that also have two valence bonds from tin to oxygen.

The catalyst employed in the invention can also be an amine or an amine derivative. Specific illustrative examples include tertiary amines such as 1,4-diazabicyclo [2.2.2]octane, bis[2-(N,N-dimethylamino)ethyl] ether, triethylamine, and the like, strong bases such as guanidine, quaternary ammonium compounds, and the like. The preferred amines are the tertiary amines.

Proton acids are also useful as catalysts in the invention. Specific illustrative examples include benzene-sulfonic acid, toluene sulfonic acid, phosphoric acid, sulfuric acid, hydrogen chloride, and the like. The arylsulfonic acids are the preferred proton acids.

Other acids that are useful as catalysts in the invention include boron trifluoride (usually as a complex with diethyl ether or an amine), titanium tetrachloride, ferric chloride, stannous chloride, stannic chloride, aluminum chloride, and the like.

A further class of useful catalysts includes the alkali metal and alkaline earth metal alkoxides and hydroxides. Specific illustrative examples of these materials include sodium methoxide, sodium ethoxide, sodium isopropoxide, potassium ethoxide, potassium butoxide, magnesium methoxide, calcium ethoxide, barium propoxide, lithium methoxide, sodium hydroxide, potassium hydroxide, lithium hydroxide, calcium hydroxide, magnesium hydroxide, and the like. The alkali metal alkoxides are preferred.

The process of the invention comprises heating a mixture of an ester-containing polymer, a filler, and a catalyst for a period of time sufficient to effect reaction between the polymer and the filler. The proportion of the components can vary widely. For example, the filler can be employed in quantities of at least about 1 weight percent, and preferably at least about 10 weight percent, based on weight of filler plus polymer. More preferred proportions of filler are found within the range of from about 20 to about 70 weight percent, based on weight of polymer plus filler. It is rare that the filler will be employed in proportions of more than about 80 weight percent, based on weight of polymer plus filler.

The catalyst is employed in catalytic quantities sufficient to promote the reaction between polymer and filler. For example, useful proportions of catalyst are found in the range of from about 0.1 weight percent, and lower, to about 8 weight percent, and higher, based on weight of polymer plus filler. Preferred proportions are found in the range of from about 0.3 to about 5 weight percent of catalyst, based on weight of polymer plus filler.

The process of the invention is carried out at an elevated temperature for a period of time sufficient to effect reaction between the polymer and the filler. For example, a reaction temperature in excess of about 90° C., and preferably in excess of about 110° C., is useful. Normally, the temperature will not be in excess of about 250° C. Reaction times of from about 5 minutes to 3 hours or more are useful. Preferred times are found within the range of from about 10 minutes to about 1 hour.

The process of the invention can be carried out by mixing the polymer, filler, and catalyst in a heated mill,

3635

Union Carbide trial exhibit UC-106: Five Union Carbide U.S. Patents on Asbestos Uses: Filled Polymers, Fire-Fighti... Published by AsbestosClaims.Law
ACL Doc 15382 · Page 4 of 30 asbestosclaims.law/library/15382/4

Banbury mixer, extruder, or the like, in order to insure ultimate mixing of the components. The mixture can then be molded, or the like, if desired, in order to produce the finished product.

The process of the invention is useful for producing molded articles having wide utility. In addition, the process of the invention can be employed to produce extruded coatings and other materials whose utility is enhanced by the improved properties that are the results of the practice of the invention.

The examples which follow illustrate various aspects of the invention.

EXAMPLES 1-34

To a 6" x 12" two-roll mill that was maintained at 120°-130° C., there was added 150 grams of Polymer A (an ethylene-vinyl acetate copolymer which has a Melt Index of 22 and which contains 28 weight percent vinyl acetate) and 1.5 grams of stearic acid (as a mill lubricant). To this polymer, there was added over a 5 to 10 minute period 150 grams of Silica A (a colloidal silica having an ultimate particle size of about 0.025 micron and having a specific surface area of about 110 square meters/gram). After the silica had been added, 5 milliliters of tetraisopropyl titanate was added. The mixture was then milled for 15 minutes at 120°-140° C. The mixture was then sheeted off and a portion was molded at 185° C. and about 5000 p.s.i. for 15 minutes. The properties of molded composition are listed in Table I, below.

By procedures analogous to that described above, a series of ester-containing polymers filled with Silica A were prepared using various catalysts. The polymers and catalysts employed were as follows:

Catalysts:

TIPT—Tetraisopropyl titanate.

OGT—Octylene glycol titanate (duPont-TYZOR OG organic titanate) (i.e., tetra[2-ethyl-1,3-hexanediol]titanate).

EGP—Triethylene diphosphite.

TPP—Triphenyl phosphite.

DPPD—Diphenyl pentaerythritol diphosphite.

D-22—Dibutyltin dilaurate.

D-14—Dibutyltin laurate maleate.

D-15—Dibutyltin dimaleate.

PTSA—p-Toluene sulfonic acid.

DABCO—1,4-diazabicyclo[2.2.2]octane.

BF_3—Boron trifluoride-etherate.

$NaOCH_3$—Sodium methoxide.

CaO—Calcium oxide.

Polymers:

Polymer A—Ethylene/vinyl acetate copolymer (Melt Index=22) containing 28 weight percent vinyl acetate.

Polymer B—Ethylene/ethyl acrylate copolymer (Melt Index=2) containing 18 weight percent ethyl acrylate.

Polymer C—Medium molecular weight poly(vinyl acetate).

Polymer D—Ethylene/butyl maleate copolymer (Melt Index=24.0, weight percent butyl maleate=30.3).

Polymer E—Ethylene/butyl fumarate copolymer (Melt Index=8.9, weight percent butyl fumarate=29.1).

Representative properties of the compositions are displayed in Table I, which follows.

TABLE I.—CATALYSTS FOR THE INTERACTION OF REACTIVE FILLERS WITH ESTER-CONTAINING POLYMERS

Example	Catalyst	Cat. Conc., percent by Wt.	Polymer	Silica Filler, percent by Wt.	Percent Polymer Insoluble in Toluene [1]	Stiffness R.T.	Modulus 150° C., p.s.i.	Tensile Strength, p.s.i.	Percent Elongation
1	TIPT	1.6	A	50	41.0	30,000	6,340	2,800	180
2	TIPT	1.6	B	50	41.2	42,000	2,940	2,370	40
3	TIPT	1.9	C	40	32.0	325,000	2,850	2,800	8
4	TIPT	1.6	70/30, A/C	50	32.8	100,000	10,000	[2] 400	8
5	TIPT	3.3	70/30, A/C	50	29.4	110,000	6,540	2,300	8
6	TIPT	4.9	70/30, A/C	50	31.6	105,000	8,850	2,495	9
7	OGT	1.6	A	50	50.2	32,000	1,885	2,750	170
8	OGT	2.1	70/30, A/C	50	30.0	60,000	4,810	2,160	16
9	EGP	2.2	A	50	29.6	44,000	7,020	2,390	180
10	EGP	2.6	C	40	25.2	195,000	9,200	880	0.4
11	TPP	2.0	A	50	42.0	32,000	6,330	1,970	220
	TPP [3]	2.0	A	50	47.2	36,000	4,090	1,950	160
12	TPP	2.1	B	45	34.5	42,000	10,100	1,800	8
13	TPP	2.0	E	50	16.4	88,000	8,180	2,625	10
14	DPPD	1.7	A	50	31.8	40,000	12,100	1,970	130
15	D-22	1.7	A	50	22.4	37,000	4,790	1,970	120
16	D-14	1.7	A	50	31.8	42,000	7,840	1,960	80
17	D-15	1.7	A	50	27.6	44,000	8,100	1,970	85
18	BF_3	1.7	70/30, A/C	50	20.2	96,000	7,080	2,050	7
19	PTSA	1.7	70/30, A/C	50	29.4	70,000	7,200	2,200	10
20	PTSA	1.7	B	50	11.2	55,000	5,200	2,450	20
21	$NaOCH_3$	1.7	70/30, A/C	50	29.2	84,000	8,120	2,200	9
22	$NaOCH_3$	1.7	B	50	27.8	57,000	6,085	2,950	32
23	$NaOCH_3$	1.7	D	45	28.1	47,000	4,185	1,760	8
24	DABCO	1.7	A	50	28.6	39,000	6,890	2,460	210
25	DABCO	1.7	B	50	27.4	85,200	4,645	1,900	80
26	CaO	1.7	A	50	25.7	34,000	3,960	2,825	150
27	$(CH_3)_4N^+OH^-$(aq) [4]	1.7	70/30, A/C	50	22.2	74,000	6,740	2,800	8
28 [2]			A	50	30.4	33,000	4,900	2,800	280
29 [2]			90/10, A/C	50	28.4	53,000	4,960	1,450	25
30 [2]			70/30, A/C	50	23.2	95,000	6,600	2,180	1
31			C	40	16.3	280,000	4,037	4,151	2
32			B	50	15.8	80,000	2,760	1,900	45
33			D	45	20.0	48,000	[5]	1,760	8
34			E	50	10.0	84,000	2,700	1,825	7

[1] Soxhlet extraction for 24 hours in refluxing toluene, percent based on weight of polymer.
[2] These samples were molded for 30 minutes.
[3] 1.7 percent of an aqueous solution containing 10 percent tetramethyl ammonium hydroxide.
[4] No load.

EXAMPLES 35-52

A series of ester-containing polymers were filled with various fillers by procedures analogous to that described above for Examples 1-34. Table II, below, displays the various ester-containing polymers, fillers, and catalysts that were employed, as well as representative properties. The fillers that were employed are as follows:

Asbestos—short fiber chrysotile asbestos.

Leached Asbestos—prepared in accordance with the following procedure: To a 5-liter three-necked, stirred flask was charged 200 gm. of chrysotile asbestos and 4,430 ml. of 1.0 N HCl. After heating (101° C.) for three hours the mixture was allowed to cool and then filtered.

A 13636

The leached asbestos was washed three times with water and dried in a vacuum oven at 60–65° C. Weight recovered=86.2 gm. This process removes substantially all the magnesium from the asbestos leaving a very porous silica residue.

Clay A—An attapulgus clay having an average particle size of 0.14 micron and a specific surface of about 210 square meters per gram.

Clay B—An attapulgus clay having an average particle size of 0.12 micron and a specific surface area of about 210 square meters per gram.

Alumina A—A powdered alumina consisting of minute fibrils of boehmite alumina. The average chemical composition is as follows: AlOOH—83.1 percent; CH_3COOH—9.8 percent; SO_4—1.7 percent; Water—5.0 percent. Alumina A has a specific surface area of 274 square meters per gram.

Alumina B—A hydrated alumina having a specific surface area of 18–24 square meters per gram and an average particle size of about 0.35–0.4 micron.

TABLE II

Example	Catalyst	Cat. Conc. (percent by Wt.)	Ester Containing Polymer	Filler (percent by Wt.)	Percent Polymer Insoluble in Refluxing Toluene	Stiffness Modulus, p.s.i. R.T.	Stiffness Modulus, p.s.i. 120° C.	Tensile Strength, p.s.i.	Percent Elongation
25			B	Asbestos (80)	12.8	25,000		1,230	470
26	TIPT	1.6	B	do	28.8	45,000		2,300	75
27	DPPD	1.7	B	do	9.8	84,000		1,880	115
28			A	do	12.0	25,000		1,140	110
29	TIPT	1.6	A	do	12.8	41,000		1,880	100
30	DPPD	1.7	A	do	12.0	34,000		1,180	180
31			A	Leached Asbestos (80)	35.2	36,000	6,230	1,600	10
32	TIPT	1.7	A	do	42.2	37,000	3,440	1,520	23
33			A	Clay A (60)	12.8	80,000	1,830	1,890	80
34	EGP	2.2	A	do	36.7	62,000	6,000	1,830	30
35			A	Clay B (80)	20.8	66,000	2,400	1,700	87
36	TPP	2.0	A	do	30.8	80,000	7,930	1,650	10
37			B	Alumina A (80)		31,000	No Load (100° C.)	1,280	35
38	TIPT	1.7	B	do		34,000	248 (100° C.)	1,240	20
39			A	Alumina B (80)		7,000	No Load (100° C.)	1,280	300
40	TIPT	1.7	A	do	9.6	9,900	52 (100° C.)	1,570	200
41			B	do	11.6	22,500	83 (100° C.)	1,300	80
42	TIPT	1.7	B	do	17.2	19,800	82 (100° C.)	1,840	80

What is claimed is:

1. A process for producing improved filled polymers which comprises heating at a temperature in excess of about 90° C. a mixture of:

(a) a thermoplastic, ester-containing polymer wherein said polymer has a polymeric chain of carbon-to-carbon bonds and wherein the ester groups are contained in side groups that are bonded to said polymeric chain,

(b) a filler in an amount of from about 1 to about 80 percent by weight based on the total weight of polymer and filler, said filler containing chemically bound water and selected from the group consisting of silica having a specific area of at least about 100 square meters per gram, and a particle size of from about 0.001 to about 0.1 micron, clay having a specific surface area of at least about 150 square meters per gram, and an average particle size of less than 1 micron, hydrated aluminum oxide having a particle size such that the largest dimension is less than about 1 micron, and asbestos, and

(c) from about 0.1 to about 8 percent by weight based on the total weight of polymer and filler of a catalyst which is a phosphite of the formula:



wherein each R individually is a member of the group consisting of hydrogen, alkyl, aryl, alkaryl, aralkyl, cycloalkyl, and alkylene phosphite, provided that at least one R is an organic group;

for a period of time sufficient to effect a reaction between said thermoplastic, ester-containing polymer and said filler, said period of time being at least about 5 minutes.

2. The process of claim 1 wherein said process is carried out at a temperature in the range of from about 90° C. to about 250° C. for a period of from about 5 minutes to about 3 hours.

3. The process of claim 1 wherein the thermoplastic, ester-containing polymer is a copolymer of ethylene with a member of the group consisting of vinyl acetate, alkyl acrylate, alkyl methacrylate, alkyl maleate, and alkyl fumarate.

4. The process of claim 1 wherein the thermoplastic, ester-containing polymer is poly(vinyl acetate).

5. The process of claim 1 wherein the phosphite is triethylene diphosphite.

6. The process of claim 1 wherein the phosphite is triphenyl phosphite.

7. The process of claim 12 wherein the catalyst is tetraisopropyl titanate.

8. Process which comprises heating at a temperature in excess of about 90° C. a mixture of:

(a) an ethylene-vinyl acetate copolymer,

(b) colloidal silica in an amount of from about 1 to about 80 percent by weight based on the total weight of copolymer and silica said colloidal silica having a surface layer of hydroxyl groups and having a specific surface area of at least about 100 square meters per gram, and a particle size of from about 0.001 to about 0.1 micron, and

(c) from about 0.1 to about 8 percent by weight based on the total weight of the copolymer and silica of a phosphite of the formula



wherein each R individually is a member of the group consisting of hydrogen, alkyl, aryl, alkaryl, aralkyl, cycloalkyl, and alkylene phosphite, provided that at least one R is an organic group; for a period of time sufficient to effect a reaction between said ethylenevinyl acetate copolymer and said colloidal silica, said period of time being at least about 5 minutes.

9. Process which comprises heating at a temperature in excess of about 90° C. a mixture of:

(a) an ethylene-vinyl acetate copolymer,

(b) colloidal silica in an amount of from about 1 to about 80 percent by weight based on the total weight of copolymer and silica said colloidal silica having a surface layer of hydroxyl groups and having a specific surface area of at least about 100 square meters per gram, and a particle size of from about 0.001 to about 0.1 micron, and

(c) from about 0.1 to about 8 percent by weight based on the total weight of the copolymer and silica of a tetraalkyl titanate;

A 13637

for a period of time sufficient to effect a reaction between said ethylene-vinyl acetate copolymer and said colloidal silica, said period of time being at least 5 minutes.

10. Process which comprises heating at a temperature in excess of about 90° C. a mixture of:

(a) an ethylene-ethyl acrylate copolymer,

(b) colloidal silica in an amount of from about 1 to about 80 percent by weight based on the total weight of copolymer and silica said colloidal silica having a surface layer of hydroxyl groups and having a specific surface area of at least about 100 square meters per gram, and a particle size of from about 0.001 to about 0.1 micron, and

(c) from about 0.1 to about 8 percent by weight based on the total weight of the copolymer and silica of a phosphite of the formula



wherein each R individually is a member of the group consisting of hydrogen, alkyl, aryl, alkaryl, aralkyl, cycloalkyl, and alkylene phosphite, provided that at least one R is an organic group; for a period of time sufficient to effect a reaction between said ethylene-ethyl acrylate copolymer and said colloidal silica, said period of time being at least 5 minutes.

11. Process which comprises heating at a temperature in excess of about 90° C. a mixture of:

(a) an ethylene-ethyl acrylate copolymer,

(b) colloidal silica in an amount of from about 1 to about 80 percent by weight based on the total weight of copolymer and silica said colloidal silica having a surface layer of hydroxyl groups and having a specific surface area of at least about 100 square meters per gram, and a particle size of from about 0.001 to about 0.1 micron, and

(c) from about 0.1 to about 8 percent by weight based on the total weight of the copolymer and silica of a tetraalkyl titanate; for a period of time sufficient to effect a reaction between said ethylene-ethyl acrylate copolymer and said colloidal silica, said period of time being at least 5 minutes.

12. A process for producing improved filled polymers, which comprises heating at a temperature in excess of about 90° C. a mixture of

(a) a thermoplastic, ester-containing polymer wherein said polymer has a polymeric chain of carbon-to-carbon bonds and wherein the ester groups are contained in side groups that are bonded to said polymeric chain,

(b) a filler in an amount of from about 1 to about 80 percent by weight based on the total weight of polymer and filler, said filler containing chemically bound water and selected from the group consisting of silica having a specific surface area of at least about 100 square meters per gram, and a particle size of from about 0.001 to about 0.1 micron, clay having a specific surface area of at least 150 square meters per gram, and an average particle size of less than 1 micron, hydrated aluminum oxide having a particle size such that the largest dimension is less than about 1 micron, and asbestos, and

(c) from about 0.1 to about 8 percent by weight based on the total weight of polymer and filler of a catalyst which is tetraalkyl titanate;

for a period of time sufficient to effect a reaction between said thermoplastic, ester-containing polymer and said filler, said period of time being at least about 5 minutes.

References Cited

UNITED STATES PATENTS

3,219,604	11/1965	Fischer	260—22
3,304,197	2/1967	Pundsack et al.	
3,350,475	10/1967	Watanabe et al.	260—865
3,377,311	4/1968	Roch et al.	260—37
3,061,577	10/1962	Pruett	260—41

OTHER REFERENCES

Schrader et al.: Modern Plastics, September 1967, Radioisotope Study of Coupling Agents in Reinforced Plastics, p. 195.

Gould: Inorganic Reactions and Structure, Holt Rinehart Winston—New York 1961, p. 127.

ALLAN LIEBERMAN, Primary Examiner

S. L. FOX, Assistant Examiner

U.S. Cl. X.R.

260—86.3, 86.7

A 10638

United States Patent Office 3,558,485 Patented Jan. 26, 1971

3,558,485

FIRE FIGHTING COMPOSITION COMPRISING AN ASBESTOS CONTAINING SLURRY

John E. Skvarla, Lewiston, N.Y., assignor to Union Carbide Corporation, New York, N.Y., a corporation of New York

No Drawing. Continuation-in-part of application Ser. No. 556,586, June 10, 1966. This application July 2, 1969, Ser. No. 838,679

Int. Cl. A62c 3/02

U.S. Cl. 252—7 3 Claims

ABSTRACT OF THE DISCLOSURE

A method of reducing the flammability of forests, shrubbery, grass and the like by coating such materials with an asbestos containing slurry.

This application is a continuation-in-part of application Ser. No. 556,586 filed June 10, 1966, and now abandoned.

This invention relates to a fire-fighting composition for use in reducing the flammability of forests, shrubbery, grass and the like. More particularly the present invention relates to the use of a "viscous water" type of fire-fighting composition which can be applied by conventional spraying and foaming techniques and which can also be applied by aerial bombardment methods.

As described in Chemicals for Forest Fire Fighting published by the National Fire Protection Asosciation in 1963, the characteristics desired in a forest fire-fighting composition include:

(a) low cost
(b) ready availability in adequate quantities in areas of primary use
(c) non-toxicity to plant and animal life
(d) good adherency to forest fuels
(e) non-dessicating to vegetation
(f) quantity requirement per gallon of water is small
(g) mixes easily and readily into a stable suspension or solution
(h) not oversensitive to either pH or mineral content of water
(i) not subject to deterioration from bacteria, enzymes, or by action with metals
(j) final characteristics are reached shortly after mixing and do not change with further standing or agitation
(k) flows through fire hoses without serious friction loss, yet sets up and holds once it is applied to forest fuels.

A particular class of fire-fighting composition which has been developed with hopes of conforming to the foregoing criteria is known as the "viscous water" group. A viscous water fire-fighting composition is defined as water which has been thickened by one or more viscosity agents and such compositions are advantageous in that in general these materials stick and cling more readily to forest fuels than plain water, they spread out in a continuous coating over fuel surfaces, and set up on a layer about three times the thickness of plan water, and on account of their greater layer thickness absorb more heat than plain water and thereby reduce the flammability of the fuel. However, previously available viscous water compositions, in spite of their advantages, have not satisfied all of the abovementioned requirements and have been found to have, in several respects, serious disadvantages. For example, previously available "viscous water" prepared through the use of organic materials are subject to bacterial action and, on account of this, loss of viscosity can occur rapidly. Also, the formation of insoluble

precipitates in the presence of certain chemicals is a common problem.

It is, therefore, an object of the present invention to provide a stable, non-deteriorating and essentially chemically inert viscous water type of fire-fighting composition which satisfies the desirable criteria set forth hereinabove.

It is another object of the present invention to provide a viscous water type of fire-fighting composition which is compatible with, and to which can be added, flame-inhibiting chemicals and foaming agents.

A fire-fighting composition for use in accordance with the present invention is a water suspension or slurry of finely divided asbestos, the asbestos content being sufficient to make the water suspension viscous. The asbestos used, which is suitably present in amounts varying from about 1 to 10% by weight of the water suspension, is chrysotile asbestos having the following properties:

Specific surface area: 60–80 $m.^2/gm.$
Magnetite content: 0.04–0.5%
Reflectance: 72–78%
Wet bulk: 750–980 ml.

This asbestos, derivable in large quantities by processing ore from the Coalinga California deposit, is commercially available from Union Carbide Corporation under the designation "High Purity Grade Asbestos" and is described in more detail in U.S. patent application 396,935 entitled "Process for Refining Asbestos and Resultant Product," the disclosure of which is incorporated herein by reference.

This patent application describes an effective process for producing asbestos having the aforementioned properties which comprises: (1) contacting asbestos ore containing asbestos, coarse rock, fine gangue and other non-asbestos impurities with water, (2) separating coarse rock and fine gangue from the remainder of the wet ore, (3) comminuting the remaining (i.e. coarse rock and gangue free) wet ore until all of the ore particles are able to pass through a screen having circular holes no larger than about 0.03 inch in diameter, (4) adding sufficient additional water to the comminuted ore to form a slurry having a solids content no greater than about 3%, (5) hydrocycloning the slurry formed in step (4), i.e., providing a hydrocycloning zone having an inlet, an overflow, and an underflow conduit, and passing the slurry through said zone at a flow rate sufficiently high to produce a centrifugal force inside said zone at least equal to 50 G's, and at the same time maintaining the ratio of the overflow rate to the underflow rate greater than about 0.5; whereby substantially pure asbestos fibers emerge in the overflow, and (6) recovering the purified asbestos fibers from said overflow.

In preparing the fire-fighting composition in accordance with this invention, dry fibers of asbestos, or pelletized fibers are slurried with water by means of the conventional beater tank or by use of the pump re-circulation loop of a storage tank. Additionally, in line mixing operations, asbestos can be injected by way of a standard solids feeder into a hose carrying water under turbulent flow conditions and a suitable slurry will be discharged from the hose nozzle and applied to forest fuels and the like. Also, as previously mentioned, the slurry can be applied to forest fuels and the like by means of aerial bombardment techniques and by foaming techniques.

By way of particular example, a 500 gallon batch of the fire-fighting composition of this invention containing 3% by weight asbestos is prepared in a conventional storage tank having a re-circulation loop by:

(1) Introducing about 450 gallons of water into the tank,

(2) Re-circulating the water through the tank under turbulent flow,

(3) Adding about 125 pounds of asbestos to the tank while the water is re-circulating.

(4) Continuing re-circulation under turbulent flow conditions to provide a complete circulation of the water-asbestos mixture. With the usual equipment this can be accomplished in a matter of minutes,

(5) Topping off the tank by adding 50 gallons of water, and

(6) Continuing re-circulation to provide one more complete re-circulating of the water-asbestos mixture under turbulent flow conditions.

By following the foregoing procedure, a stable water slurry of asbestos characterized by a gelatinous structure is quickly obtained which has a high viscosity and which remains stable indefinitely and can be readily applied to the surfaces of forest fuels by conventional spraying, foaming and aerial bombardment techniques.

Slurries of water and asbestos in accordance with the present invention can be adjusted with respect to viscosity by varying the asbestos content. All water-asbestos slurries of this invention are characterized by a gelatinous structure created by the colloid-like asbestos fibers (which are about 200–300 angstroms diameter and 0.25–10 microns in length) and Table I shows the viscosities obtained with different amounts of asbestos.

TABLE I.—VISCOSITY OF WATER-ASBESTOS SLURRIES OF THIS INVENTION, MEASURED BY BROOKFIELD MODEL LVF HELIPATH VISCOMETER

	Brookfield spindle designation	R.p.m.	Viscosity, centipoises
Asbestos, percent by weight:			
1	T-A	6	≥1,000
2	T-C	6	10,000
4	T-D	6	25,000
8	T-F	6	132,000

A particular advantage of the present invention is that its high viscosity provides exceptionally good adhesion to forest fire fuels. To illustrate this feature, identical wooden blades of known surface area representing forest fuel material were dipped into plain water and various asbestos-water sample slurries of this invention and thereby coated and the weights of retained material were measured and compared by calculating a slurry/water ratio as follows:

$$S/W = \frac{\text{Weight increase of blade dipped in sample}}{\text{Weight increase of blade dipped in water}}$$

The results shown in Table II indicate the weight of an adhering film on the wooden blades and thus the thickness of the film for various compositions of this invention as compared to water. The thickness of the film indicates the effectiveness of the slurry in reducing the flammability of the fuel material.

TABLE II

Sample (percent asbestos by weight):	S/W
0 (plain water)	1
1	2.0
2	3.6
3	6.4
4	8.4
5	9.1
6	10.7

A further advantage of the asbestos-containing composition used in the practice of this invention is that it is capable of retaining large amounts of water within its characteristic gelatinous structure and this provides increased opportunity for water penetration which is important in fighting the so-called "duff" fires and under other circumstances. This feature is of particular importance since most if not all previously known "viscous water" type compositions do not have this capability.

The data of Table III illustrates this aspect of the present invention and shows the relative amounts of free and retained water for asbestos slurries of this invention when placed on a 100 mesh screen and allowed to drain for 5 minutes.

TABLE III

	Water retained in slurry	Free water
Percent by weight asbestos in slurry:		
1	47	53
2	68	32
3	74	26
4	79	21
8	85	15

The composition of the present invention is additionally advantageously characterized by pseudo plastic flow characteristics which yield flow rates shown by the test results of Table IV for a 3% asbestos-water composition of this invention through a 1-inch (inside diameter) hose.

TABLE IV

Flow rates, 3% asbestos slurry through 100 feet of 1 in. I.D. rubber hose

Flow, gal./min.:	Pressure, p.s.i.g.
10	24
20	30
30	34
35	36
40	47

To further illustrate the properties of the water-asbestos compositions of this invention Table V shows a comparison of flow rates through a one-inch I.D. hose of various asbestos-water slurries with respect to plain water.

TABLE V

	Flow velocity, ft./sec.	Percent of plain water flow velocity for same pressure
Asbestos-water composition:		
2.5% asbestos	10	28
Do	15	78
3.4% asbestos	12	22
Do	16	85
4.2% asbestos	18	20
Do	20	60

In addition to the foregoing advantages it has been also found that on account of the aforementioned small fiber size and high purity of the asbestos addition, that the asbestos-water composition in accordance with this invention can be used with all standard fire-fighting equipment without danger of erosion or plugging.

By way of example, Table VI shows the relative abrasiveness of the asbestos addition of this invention as compared to other materials.

TABLE VI

Relative abrasion factors

Asbestos addition material	1
Bleached sulfite pulp	2
Diatomite	10
Bentonite clay	39

The foregoing Table VI shows for example that the asbestos is only one-half as abrasive as sulfite pulp and one-tenth as abrasive as diatomite. The method and equipment for making the measurements of Table VI were described and published in the Proceedings of the Conference on "Nuclear Applications to the Wood, Paper and Pulp Industries." The conference was held Apr. 23–24, 1964, and was sponsored by the Institute of Technology of Washington State University and the Division of Isotopes Development of the U.S. Atomic Energy Commission.

UC 0470

Published by AsbestosClaims.Law
asbestosclaims.law/library/15382/9

In a further embodiment of the present invention, one or more fire-retardant and/or fire-suppressing chemical additives, such as ammonium sulfate, ammonium phosphate and ammonium chloride can be added to the asbestos-water composition to provide long-term fire protection. Also, wetting agents such as commercial detergents, e.g., Tergitol,[1] can be used with the asbestos-water composition, with or without chemical additives to provide increased penetration of the fuel upon release of "free water" from the slurry.

The aforementioned fire-fighting compositions can be easily prepared, for example by dry blending the asbestos with the chemical additive and if desired other materials such as vegetation coloring dyes and corrosion inhibitors. The dry mix can then be converted to an aqueous slurry by the techniques previously described.

The following Tables VII(a) and VII(b) show suitable compositions in accordance with the present invention containing chemical additives.

TABLE VII(a).—AQUEOUS SLURRIES

Asbestos, weight percent:	Additive	Percent by weight additive
1-10	Ammonium sulfate	5-35
1-10	Ammonium phosphate	5-35
1-10	Ammonium chloride	5-35

to produce stable foams of high strength with low drain rates. Only relatively small amounts of foaming agent are required, and conventional foaming techniques can be used.

The following Table VIII shows test results of foams prepared in accordance with the present invention. In obtaining the data of Table VIII, a 100 ml. solution of water or asbestos-water slurry was made with the indicated foaming agent. The solution was agitated for 30 seconds and the volume of foam produced was compared to the original 100 ml. volume and the ratio recorded as the Foam Ratio. The foam was observed and the times noted at which 25% (25 ml.) and 50% (50 ml.) of solution had come out of the foam. It can be seen from Table VIII that the compositions of the present invention produce stable long lasting foams.

A further test was performed by placing a portion of the foams produced on surfaces of kerosene and acetone to determine the effectiveness of the foams with the respective type of fuels represented by these materials. A "Y" in Table VIII indicates that the foam did not break down and shows the foam to be effective against fires supported by the material specified. Of particular significance is the finding that with the use of foaming agents (1) and (2) with an asbestos-water slurry of this invention, a foam is obtained which is "compatible," i.e., stable, in the presence of both the "kerosene," i.e., hydrocarbon and "acetone," i.e., polar type fuels.

TABLE VIII.—COMMERCIAL FOAMING AGENTS AND ASBESTOS MIXTURE

Foaming agent*	Percent by wt. foam agent	Percent by wt. asbestos	Drain Time, min. 25%	Drain Time, min. 50%	Foam ratio	Compatibility with— Kerosene	Compatibility with— Acetone
(1) Unox	2	0	.....	3	6	Y	.....
	1	1	.....	5	5	.....	Y
(2) Apex	2	0	.....	5	4	Y	.....
	1	1	.....	9	3	Y	.....
	1	2	15	25	2	Y	Y
(3) National 99	3	0	2	6	4	Y	.....
	1	1	27	.....	2	Y	Y
(4) National 3% cold	3	0	6	.....	5	.....	.....
	1	1	5	.....	3	Y	.....
	1	2	15	.....	2	Y	.....
(5) National 3% regular	3	0	2	.....	5	Y	.....
	1	1	10	.....	3	Y	.....
	1	2	80	.....	2	Y	.....
(6) National 6% regular	3	0	2	4	5	Y	.....
	1	1	11	25	3	Y	.....
	1	2	19	.....	2	Y	.....
(7) Petrojet	3	0	2	4	5	Y	.....
	1	1	14	25	2	Y	.....
	1	2	25	.....	2	Y	.....

*Commercially available under these names:
(1) Trademark of Union Carbide Corp. (anionic type).
(2) Protein based.
(3) Product of National Foam Systems Inc.
(4) Product of National Foam Systems Inc.
(5) Product of National Foam Systems Inc.
(6) Product of National Foam Systems Inc.

A-3541

TABLE VII(b).—DRY MIX

Additive:	Weight of additive/ weight of asbestos
Ammonium sulfate	1-70
Ammonium phosphate	1-70
Ammonium chloride	1-70

A still further embodiment of the present invention involves the use of foaming agents with the asbesto-water composition, with or without chemical additives. Nonionic, anionic, cationic, and protein type commercially available foaming agents have been employed and found

[1] Trademark of Union Carbide Corporation.

In addition to the above-mentioned advantages, the asbestos-water composition of this invention has been found to be unaffected by the pH or mineral content of the water. Also, the composition is non-toxic to plant and animal life; its final characteristics are attained shortly after the mixing of asbestos and water, and the asbestos-water composition can be stored indefinitely.

The parameters specific surface area, magnetite content, reflectance and wet bulk, previously mentioned hereinabove, are defined as follows:

Specific surface area is calculated from adsorption data using the BET (Brunauer, Emmet, Teller) method as described in Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press (1945).

Published by AsbestosClaims.Law
asbestosclaims.law/library/15382/10

Magnetite content is measured by a permeametric device patterned after ASTM standard method D–1118–57 and modified with respect to sensitivity to measure a limit of detection of 0.005% magnetite, and the range extended to measure 0.10% magnetite in the mid-scale of the instrument.

Reflectance is measured on a sample prepared according to TAPPI (Technical Association of the Pulp and Paper Industry) standard T–452–m–58 and reported as percent of ultimate reflectance based on magnesium oxide as 100% reflectance.

Wet bulk is a measurement of the terminal settled volume which a given weight of an asbestos suspension will have at the end of a specified period of time. It is also a practical indication of the completeness of the fiberization or openness of the asbestos. The specific test is as follows: 2 grams of asbestos are placed in a graduated cylinder containing 1000 ml. of distilled or demineralized water. The cylinder is then gently inverted and returned to an upright position 10 times and then placed on a reasonably vibration free bench. The level of the asbsetos suspension (clear water interface) is read at the end of one hour. The volume of suspension is the "wet bulk."

What is claimed is:

1. In a method of treating forest fuels material to reduce the flammability thereof by coating said material with a film of water, the improvement which comprises coating said material with a slurry consisting essentially of a suspension of finely divided asbestos in water wherein the asbestos constitutes between about 1 and

10 percent by weight of the suspension and is characterized by the following:

Specific surface area: 60–80 $m.^2/g.$
Magnetite content: 0.04–0.5%
Reflectanceff 72–78%
Wet bulk: 750–980 ml.

2. A method in accordance with claim 1 wherein said slurry additionally contains a dissolved water-soluble fire-suppressing substance selected from the group consisting of ammonium sulfate, ammonium phosphate and ammonium chloride.

3. A method in accordance with claim 1 wherein said slurry additionally contains a foaming agent dispersed therein.

References Cited

UNITED STATES PATENTS

2,551,919	5/1951	Williamson et al.	169—14
2,652,325	9/1953	Novak	252—313X
2,661,287	12/1953	Barbaras	252—313X
2,880,172	3/1959	McCutchan	252—2
2,901,428	8/1959	Schulenburg	252—2X
3,196,108	7/1965	Nelson	252—2X
3,445,384	5/1969	Schreiber	252—2

JOHN T. GOOLKASIAN, Primary Examiner

D. J. FRITSCH, Assistant Examiner

U.S. Cl. X.R.

252—2, 3, 4, 8.1

A-3642

Published by AsbestosClaims.Law
asbestosclaims.law/library/15382/11

United States Patent

[11] 3,619,354

[72] Inventor Robert G. Woolery
Lewiston, N.Y.

[21] Appl. No. 796,913
[22] Filed Feb. 5, 1969
Continuation-in-part of Ser. No. 576,248, Aug. 31, 1966, abandoned
[45] Patented Nov. 9, 1971
[73] Assignee Union Carbide Corporation
New York, N.Y.

[54] LAMINATED FELTED SHEETS AND ASBESTOS CONTAINING COATING COMPOSITION FOR USE THEREIN

3 Claims, No Drawings

[52] U.S. Cl. 162/129, 117/28, 117/140, 161/156, 161/205, 162/153, 162/155
[51] Int. Cl. B32b 5/08, B32b 19/06, D21h 5/18
[50] Field of Search 162/3, 127, 129, 132, 133, 153, 201, 186; 161/155, 156, 205; 117/140, 28, 126; 106/63

[56] References Cited

UNITED STATES PATENTS

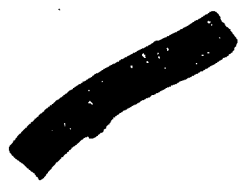
367,424	8/1887	Merrill	162/129
1,558,495	10/1925	Overbury	162/129
2,626,213	1/1953	Novak	161/205 X
2,881,072	4/1959	Clark	162/201 X
2,927,038	3/1960	Schulz	117/140 X
2,993,802	7/1961	Cascone	162/129 X
3,246,767	4/1966	Pall et al.	117/140 X

OTHER REFERENCES

Paper Trade Journal (Feb. 14, 1966) pg. 40-4, " New Type of Asbestos Shows Advantages in Papermaking" Ingalls et al.
" Pulp and Paper," Casey, James P., Interscience Publishers, N.Y. (1961), p. 1553-4 Vol. 3

Primary Examiner—S. Leon Bashore
Assistant Examiner—Alfred D'Andrea, Jr.
Attorneys—Paul A. Rose, Thomas I. O'Brien, Frederick J McCarthy, Jr., Robert C. Cummings and Lawrence G Kastriner

ABSTRACT: Disclosed is a process for forming laminated felted sheets wherein a wet base sheet of fibrous material is formed on a paper making screen and, before the wet base sheet is removed from the screen, a nonseparable, uniform asbestos-binder composition is applied thereto. The composition comprises an intimitate mixture containing (a) at least 50 percent by weight of chrysotile asbestos having a specific surface area from about 60–80 $m^2/g.$, a magnetite content of from about 0.04–0.5 percent, a reflectance of from about 72–78 percent, and a pulpability such that 0.2–1 percent of the asbestos is retained on a 65 mesh Tyler screen and (b) a binder therefore. The ratio of asbestos to binder, on a dry weight basis, ranges from about 3:1 to 9:1.



A 10343

LAMINATED FELTED SHEETS AND ASBESTOS CONTAINING COATING COMPOSITION FOR USE THEREIN

The desirability of adding a binder to nonwoven felted sheets has been known for a long time, and numerous binders have been used for this purpose, for example, natural and synthetic resins, gums starches, waxes and various rubbery latices. In accordance with prior art methods these binders have been incorporated into the felted fibrous materials in one of three ways. The most common way of incorporating the binder is to mix it with the fibrous furnish composition and then lay and dewater the mixture on a conventional Fourdrinier screen or cylinder machine. This type of process suffers from a variety of difficulties, the most important of which is improper coagulation and self-agglomeration of the binder causing weakness and lack of uniformity in the paper.

Another way of incorporating binders into felted fibrous sheets has been the practice, disclosed, for example, in U.S. Pat No. 2,022,687, of first forming a fibrous web upon a paper-making machine and thereafter impregnating the web, while supported on the paper-making screen, by passing it through a permeating bath containing the binder material. This practice suffers from the disadvantage of requiring a separate saturating machine, as well as difficulty in controlling the amount of binder added to the original sheet. Neither of the above-described methods serves to produce a laminated or coated structure, but rather produces a more or less imperfectly impregnated sheet.

A laminated sheet can, of course, be made by simply coating the surface of finished paper with a rubber, resinous or waxy binder. Such products, however, tend to have poor adhesion between the coating and the paper.

It has long been desirable to produce a paper product which contains on at least one side thereof a coating of a binder which is integrally bound to and substantially inseparable from its paper base sheet, i.e. to produce a laminated product wherein the lamina will not separate, and to be able to apply such coating to the base sheet simply, economically and without the need for additional complex machinery.

OBJECTS

It is an object of this invention to produce a coated nonwoven felted fibrous sheet containing on at least one surface thereof a substantially nonseparable uniform and smooth rubbery, resinous or waxy coating.

It is another object of this invention to provide a process for applying to at least one surface of a felted fibrous base sheet, a resinous, rubbery or waxy coating by use of conventional paper-making machinery.

It is yet another object of this invention to produce a composition suitable for coating nonwoven felted fibrous base sheets, such as paper and the like, which coating will be integrally bonded to said base sheet and form a uniform, smooth coating thereon

DESCRIPTION OF INVENTION

The above mentioned and other objects which will become apparent from the detailed description to follow are achieved by a process comprising the steps of (1) providing a base sheet of felted fibrous material on a paper-making screen, and prior to removal of said base sheet from the screen, (2) applying on top of said base sheet a composition comprising an intimate mixture of chrysotile asbestos fibers having certain critical properties (hereafter defined) and a binder therefor.

Another aspect of this invention consists of a laminated product consisting essentially of a felted fibrous base sheet and integrally bonded thereto a coating or lamina; the latter comprising an intimate mixture of chrysotile asbestos having certain critical properties (hereafter defined) and a binder therefor.

A third aspect of this invention consists of a composition, suitable for coating nonwoven felted sheets, comprising an intimate mixture of chrysotile asbestos fibers having certain critical properties (hereafter defined) and a binder therefor. Said composition, which may also be used to form a self-supporting sheet, may if desired, include optional ingredients such as conventional paper-making fibers, fillers, pigments, dyes and the like.

To be suitable for purposes of this invention the asbestos used must have the following critical properties:

specific surface area	60–80 m²/g
Magnetite content	0.04–0.05%
Reflectance	72–78%
Pulpability	0.2–1.0%

Asbestos having the aforementioned properties is commercially available as high purity grade Calidria*

*Trademark of Union Carbide Corp asbestos

The properties of the asbestos material set forth above are critical in the sense that only by use thereof are the desired results of the invention obtained.

Specific surface area is calculated from adsorption data using the BET (Brunauer, Emmet, Teller) method as described in Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press (1945).

Magnetite content is measured by a permeametric device patterned after ASTM standard method D–1118–57. Since the lower limit of detection of the ASTM device is only about 0.20 percent magnetite, the ASTM method has been improved with respect to sensitivity to measure a limit of detection of 0.005 percent magnetite, and the range of measurements has been extended to measure 0.10 percent magnetite in the midscale of the instrument. In order to obtain this greater range and improved sensitivity, the ASTM method has been modified to detect the phase changes of the current generated when magnetic materials are placed in the transformer core rather than the voltage changes generated.

Reflectance is measured on a sample prepared according to TAPPI (Technical Association of the Pulp and Paper Industry) standard T–452–*m*–58 and is reported as percent of ultimate reflectance based on magnesium oxide as the standard of 100 percent reflectance.

The pulpability of the high purity asbestos must be such that less than 1.0 percent and preferably less than 0.5 percent is retained on a 65-mesh Tyler screen when measured in accordance with the procedure described below. The term "+65 —mesh" is used to mean the amount, expressed as the percent of the sample, which does not pass through but is retained on a 65-mesh Tyler screen The measurements are made on a wet pulped sample rather than a dry sample, since the particle size under wet pulped conditions is significant for purposes of paper manufacture. The pulpability is determined by adding 40 g. of asbestos and 2 liters of water to a TAPPI Standard Disintegrator and agitating the mixture for 4 minutes. A 250 ml. aliquot sample is then taken from the disintegrator and diluted to 3 liters with water. The diluted slurry is then poured through a 65-mesh (Tyler standard) wire screen held at an angle of about 30° from the horizontal position. The oversize remaining on the screen is washed back into a 4 liter beaker diluted with water and poured through the screen again as before. The oversize remaining is then backwashed, diluted and poured over the screen a third time. The oversize remaining is then dried at about 105° 50 C. and weighed The net weight of the oversize multiplied by 20 is the percent +65-mesh asbestos material contained in the original sample. This is the value referred to as the "Pulpability."

Table I below illustrates the differences in the properties of the closest chrysotile asbestos of the prior art and the chrysotile asbestos essential for use in the present invention Although Coalinga chrysotile* asbestos is preferred as the source of the asbestos, any chrysotile asbes[redacted]

A 13644

*Coalinga chrysotile asbestos is mined from a large deposit near Coalinga, California

Published by AsbestosClaims.Law
asbestosclaims.law/library/15382/13

for use in this invention, provided it has the critical properties defined above.

TABLE I.—COMPARATIVE PHYSICAL PROPERTIES OF ASBESTOS FIBERS

Type of asbestos	Percent reflectance	Percent magnetite	Specific surface area, m.²/gm.	Pulpability percent +65 mesh
Canadian chrysotile	55–70	3.5–4.5	10–31	10–20
Conventional coalinga chrysotile	60–64	1.0–3.0	55–59	10–67
Required for invention	72–78	0.04–0.5	60–80	0.2–1.0

Binders which are useful in the preparation of the coating composition of this invention include all of the common sizing agents used in the paper industry, such as animal glues, starches, gelatin, rosin, rosin derivatives, waxes, bituminous materials such as asphalts, tars, pitches and bituminous as well as resinous and rubbery lattices.

Synthetic, resinous and rubbery lattices are the preferred binders. Illustrative suitable rubbery lattices are copolymers of butadiene and styrene (i.e. GR–S rubber containing 50–80 percent by weight butadiene), copolymers of butadiene and acrylonitrile (i.e. Buna—N—or Hycar rubber containing 50–80 percent butadiene), polychloroprenes (i.e. neoprenes), homopolymers of butadiene, butadiene-isoprene copolymers, and terpolymers of butadiene, styrene and acrylic acid or lower alkyl acrylites.

Illustrative resinous binders which are useful are thermosetting resins such as phenol aldehyde resins, and melamine formaldehyde resins. Suitable thermoplastic resin binders include, for example, vinyl and substituted vinyl resins such as polyvinylchloride, polyvinylacetate, polyvinylacetal, polyvinylalcohol, polystyrene, polyacrylates, polymethacrylates, polyacrylonitrile, polyacrylamide and copolymers of these materials. Any resinous binder is useful for depositing the asbestos of this invention onto a base sheet, as long as it is dispersible in an aqueous medium or suspendible therein in particulate form.

The coating composition is prepared by first dispersing the asbestos in an aqueous slurry by means of a high shear device; for example, a Reitz disintegrator, a Fitzmill or a waring blender. The binder, usually in an aqueous suspension, is then blended in with the asbestos using low shear mixing such as obtained with an ordinary mixer.

The concentrations of both the asbestos slurry and the binder suspension are ordinarily kept below about 3 percent solids by weight, since at higher concentrations the composition becomes too viscous for easy handling. The proportions of asbestos to binder are controlled to give optimum efficiency in terms of the retention of the solids on the paper-making screen. The asbestos content, however, must be sufficiently high to insure that its cationic charge will be adequate to coflocculate all the other solid components of the mixture. If the concentration of the binder is too high, the binder in excess of that which the asbestos can flocculate will in large part be lost by draining through the base sheet into the white water. The optimum proportions of asbestos to binder will vary depending upon the particular binder and other additives used. Preferably, the ratio of asbestos to binder (on a dry weight basis) is from 3:1 to 9:1. The same proportions are useful whether the composition is to be used for coating purposes or for making an extruded, self-supporting film. Self-supporting films of this composition have the properties of an asbestos filled plastic film, and can be used, for example, as packaging film or as wallpaper.

The asbestos-binder coating composition may contain additives such as fillers pigments or fibrous materials. The use of TiO_2 and clay are illustrated below, however, any conventional paper making fillers and/or pigments may be used, as well as mixtures thereof. Furthermore, fibrous materials other than asbestos, both synthetic and natural, may also be included, if desired, in the coating composition. For example, one or more natural or synthetic mineral or vegetable fibers may be added to the composition. In all such cases, however, the weight of asbestos having the critical characteristics previously described must be at least 50 percent of the weight in the composition. The asbestos in such a coating composition is believed to act as a coupling agent between the binder and the other fiber or nonfibrous additives, since the cationic nature of the asbestos is believed to be attracted by the other fibers, the nonfibrous additives, as well as the latex binder, all of which are anionic in character. The binder is preferably added after the asbestos and additive have been adequately mixed, since the asbestos will cause the binder to coagulate.

The asbestos-binder composition of this invention is novel and unusual in that it can be applied directly on top of a wet base sheet before the sheet is taken off the paper-making screen. Such "on the wire coating" has not previously been feasible because coating formulations tried in the past have drained through the base sheet. Use of asbestos having the critical properties previously defined "holds out" the coating composition from the base sheet, and enables the binder composition to be applied directly onto the paper making screen containing the wet base sheet. Furthermore, there is no need for using organic surfactants, wetting agents, dispersing agents, or other flocculating agents required by prior art methods to obtain flocculation and deposition of a binder onto the fibers. The critical properties of the above described asbestos itself assure both proper coflocculation of the binder onto the asbestos and deposition of the asbestos-binder coating onto the base sheet.

Any felted product which can be prepared on a paper making screen can be used as the base sheet in the present invention. These felted products can be formed from organic, inorganic or mixed materials. Paper base sheets are preferred. As used throughout the specification and claims of this disclosure the term "paper" is used in its generic sense, i.e. to include any nonwoven, felted fibrous sheet, including but not restricted to bond, wrapping, tissue, printing, wall and backing paper as well as cardboard, wallboard, millboard, and the like.

Suitable inorganic fibrous materials for base sheets include glass wool, mineral wool, and silicate fibers. Useful organic fibers include, for example, cotton, silk, hemp, ramie, alpaca, hair, fur and animal bristles. Useful synthetic organic fibers are fibers made from polyamides, acrylates, polyesters, cellulose acetate, regenerated cellulose (rayon), polyvinyl chloride, polyethylene, polyurethane, polytetrafluoroethylene and the like.

Preferred base sheets are those made from conventional cellulosic pulp used for the manufacture of paper for example, mechanical, semichemical, sulfite, sulfate, or craft (soda) pulp. Mixtures of cellulosic pulp or mixtures of cellulosic and noncellulosic fibers may also be used.

The paper base sheet useful in this invention may have included in it conventional fillers such as, for example, clay, sodium silicoaluminate, diatomaceous silica, calcium silicate, talc, calcium carbonate, calcium sulfate, barium sulfate, zinc sulfate and titanium dioxide. Such fillers may be incorporated not only into the base sheet, but also into the asbestos coating composition of this invention, if desired.

In general, a base sheet is made by first preparing a dilute aqueous pulp of suspended fibers, incorporating into the pulp desired additives such as fillers or pigments to make a paper furnish composition, depositing the furnish composition from a head box onto a moving fine mesh screen, and then draining the excess water through the screen. The asbestos-binder coating composition of this invention is then applied directly onto the wet felted fibrous web or sheet while the latter is still moving on the paper making screen. The coating step is conveniently carried out by having a second head box from which the coating composition is applied onto the wet base sheet on the screen.

A13645

EXAMPLES 1–12

Two-ply laminated sheets consisting of a cellulosic base sheet with a coating of asbestos and binder were prepared on a laboratory Noble and Wood handsheet machine using the following procedure. A base sheet having a basis weight of 60 g./m² was first prepared by adding unbleached craft pulp to the deckle box of the handsheet machine and allowing it to drain almost completely. Then a second composition consisting of a mixture of binder and asbestos having the critical properties heretofore defined was poured on top of the base sheet which was still in the deckle box. The proportions (on a dry weight basis) of asbestos to binder used are given in table II below. In examples 1 through 7 the binder used was an aqueous dispersion of a synthetic late of a copolymer containing about 60 percent styrene and 40 percent butadiene. In examples 8 through 12 the binder used was an aqueous dispersion of a copolymer containing about 40 percent styrene, 5 percent acrylic acid and 55 percent ethylhexyl acrylate. The asbestos latex coating composition contained about 1 percent solids. It was added to the deckle box slowly in order to minimize the disturbance of the wet cellulosic base sheet. The deckle box was then allowed to drain completely. The laminated sheet was then removed from the deckle box, pressed with a felt press, and dried in a drum dryer operated at a temperature of about 105° C. The heat of the drier not only dried the laminated sheet but also cured the latex.

Twelve samples were prepared in the manner described above and tested to determine optimum retention of the coating, as well as the physical properties of the laminates produced.

The data from table II demonstrates that optimum retention of the coating is achieved when the ratio of asbestos to latex (on a dry weight basis) is from 80.20 to 90.10, in other words, when about 10–20 percent of the asbestos latex composition is latex and 80–90 percent is asbestos. The data above also demonstrates that in general the best physical properties are obtained when there is maximum retention of the coating.

EXAMPLES 13–22

The following examples demonstrate the method of making a two-ply laminated paper, in accordance with the invention, on a continuous paper-making machine by using a secondary head box on a conventional Fourdrinier machine. The base sheets were made from a furnish containing 50 percent wood and 50 percent bleached soft wood sulfate pulp. The sulfate pulp was refined to a freeness of 370 and the freeness of the mixture of ground wood and sulfate was 250. The only additive used in the base sheet furnish was alum, added in sufficient amount to give a pH of 4.5 at the first headbox. The first headbox contained the furnish composition for the base sheet, and the secondary headbox contained the coating composition for the cop laminate.

Three different furnishes were used in the secondary headbox for laying down the top ply of the two-ply paper. The first top ply coating composition, labeled composition A in table III below, consisted of 85 percent asbestos and 15 percent latex. The second top ply coating composition, labeled composition B in table III below, consisted of 40 percent asbestos, 40 percent clay and 20 percent latex. The third top ply coating composition, labeled composition C in table III below, consisted of 52.8 percent asbestos, 27.2 percent TiO_2 and 20 percent latex. All of the coating compositions were applied as 1 percent solids slurries directly onto the wet base sheet as it moved continuously along the Fourdrinier wire. The asbestos used had the critical properties set forth above. In all cases the latex used was an aqueous dispersion of a copolymer containing about 60 percent styrene and 40 percent butadiene.

One objective of this series of experimental runs was to make the top layer as heavy as possible, and to apply it onto a light base sheet as well as onto a heavy base sheet. Changes in the thickness of both the top ply and the bottom ply were made by setting the flow rate from a headbox at a steady rate and then adjusting the speed of the Fourdrinier wire. Once a base sheet had been run long enough to insure steady state conditions, the flow of top ply furnish was started from the second headbox and increased slowly until the wet web appeared to be just on the verge of breaking between the couch roll and the first press. Under these conditions the run was continued for 10 to 15 minutes. Thereafter the wire speed was changed, and the procedure repeated with a different top ply or coating furnish.

Samples of paper were taken from each set of runs and cut into sheets. Some of the sheets from each set were calendered at room temperature and some at approximately 230° F. After conditioning at a constant temperature and humidity room critical wax tests were made on the calendered sheets, as well as on uncalendered samples of sheet. The results of the critical wax tests are shown in table III below.

The critical wax tests were conducted in accordance with TAPPI standard test T–459 su–65. This test consists of taking a standard series of wax sticks, each having a different hardness, heating them to their melting point and [illegible] each of the sticks to the paper sheet. The number of the

TABLE II

	Ratio of asbestos to latex	Top laminate retention (percent)[1]	Percent reflectance[2]	Tensile strength Dry (lbs.)	Tensile strength Wet (oz.)	H_2O adsorption[3] (minutes)	Oil adsorption[4] (minutes)
Example							
1	[illegible]	[illegible]	21	16.[illegible]	12.8	0.7	16.6
2	80:20	67	41	11.3	25.6	6.6	51.0
3	60:40	81	42	14.7	24.6	10.8	77.0
4	70:30	88	43	14.2	25.0	13.0	100.0
5	80:20	96	52	16.4	28.7	27.0	63.0
6	90:10	95	57	18.3	30.4	6.8	56.0
7	100:0	84	55	7.4	6.4	2.0	19.0
8	80:20	81	51	13.8	10.7	4.7	36.0
9	60:40	81	64	14.9	15.7	10.6	32.0
10	70:30	77	64	14.1	13.9	10.3	51.0
11	80:20	84	62	15.0	15.7	22.0	40.0
12	90:10	95	61	12.9	16.6	20.6	44.0

[1] Top laminate retention is the percent asbestos-latex retained based on the quantity applied to the base sheet.

[2] Percent reflectance was determined with a photovolt meter according to TAPPI standards.

[3] H_2O adsorption was determined by placing a drop of water on the surface of the sheet and recording the time in minutes for the water to be adsorbed.

[4] Oil adsorption was determined in the same manner as water adsorption, using one drop of oil.

Union Carbide trial exhibit UC-106: Five Union Carbide U.S. Patents on Asbestos Uses: Filled Polymers, Fire-Figh… Published by AsbestosClaims.Law
ACL Doc 15382 · Page 15 of 30 asbestosclaims.law/library/15382/15

TABLE III

Example	Wire speed (f.p.m.)	Top ply	Basis weight, (grm./m.)	Weight ratio top ply: base ply	Critical wax number: Uncalendered	Calendered room temperature	Hot calendered 220° F.
19	40	A	117	.86	6	6	7
14	25	B	184	.41	7	10	11
15	30	B	100	.35	6	9	20
16	35	B	126	.91	6	8	11
17	40	B	88	.76	7	7	10
18	50	B	105	1.05	8	9	10
19	20	C	109	.26	10	10	11
20	35	C	83	.23	10	10	11
21	45	C	99	.35	8	9	10
22	75	C	79	.20	6	9	10

highest numbered stick that does not pull fibers from the surface is the critical wax value of the paper. It can be seen from table III that very good bonding between the plies was obtained as indicated by the critical wax numbers ranging from 6 to 11 Some increase in critical wax was obtained by calendering the sheet, with hot calendering giving the best results. The tests also indicate that an increase in the ratio of latex to asbestos and pigment increases ply bonding.

The laminated paper of the present invention has numerous advantages not possessed by prior art materials, such as improved ply bonding and low cost of manufacture due to the fact that separate equipment for coating is not required. The coated paper of the present invention is particularly useful for one side "hold out" items such as paper plates, drinking cups, flexible packaging and the like.

I claim:

1. A process for the manufacture of laminated sheets comprising the steps of:

1. forming on a paper making screen, a wet base sheet of felted fibrous material and prior to removal of said base sheet from said screen

2. providing a nonseparable, uniform, asbestos-binder coating on the surface of said base sheet by applying on top of said wet base sheet before said wet base sheet is removed from the paper-making screen a composition comprising an intimate mixture containing at least 50 percent by weight of chrysotile asbestos characterized by a specific surface area between about 60 to 80 $m^2/gm.$, a magnetite content of from about 0.04 to 0.5 percent, a reflectance of about 72 to 78 percent and a pulpability such that 0.2 to 1 percent of the asbestos is retained on a 65-mesh Tyler screen and a binder therefor, the ratio of asbestos to binder, on a dry weight basis, being from about 3:1 to 9:1.

2. The process of claim 1 wherein the coating composition applied on top of said base sheet contains an additive selected from the group consisting of fibrous materials, fillers, pigments and mixtures thereof.

3. The process of claim 1 wherein the base sheet is paper.

* * * * *



A 13647

United States Patent Office

3,677,803
Patented July 18, 1972

3,677,803

ANTISEIZE THREAD COMPOSITION

Frank W. Bennett and Loren S. Van Delinder, Charleston, W. Va., assignors to Union Carbide Corporation, New York, N.Y.

No Drawing. Original application Aug. 30, 1968, Ser. No. 756,355. Divided and this application Mar. 5, 1971, Ser. No. 121,534

Int. Cl. B44d 5/00, 5/08

U.S. Cl. 117—94 11 Claims

ABSTRACT OF THE DISCLOSURE

An antiseize composition comprising finely divided pulverized chrysotile asbestos and a carrier therefor. There is also provided a process for treating metallic securing assemblies of the type wherein a metallic securing member such as a stainless steel bolt threadably engages a fastening element such as a stainless steel nut to prevent seizure of the fastening element to the securing member at the site of threadable engagement which comprises applying the novel antiseize material to the portions to be in threadable engagement.

This application is a division of application Ser. No. 756,355, filed Aug. 30, 1968, now abandoned.

The present invention relates to a process for treating metallic securing assemblies of the type wherein a metallic securing member threadably engages a fastening element and more particularly to a process for treating bolts to prevent seizure of the bolts to the nut in threadable engagement therewith.

Securing assemblies fabricated from metals such as steel and/or stainless steel bolts and nuts, threaded rods and the like are currently widely employed in many commercial and industrial applications. Their wide acceptance is based primarily on the relative strength provided by such metals, particularly steel and stainless steel assemblies, and also their resistance to many chemical reactions. However, these securing assemblies, for example, steel bolts when used at high temperatures, tend to weld to the nut with which it is in threadable engagement so that either the threads are damaged during disassembly or complete seizure occurs requiring that the bolts be twisted or cut off. When employing austenitic stainless steel bolts, the problem is even more pronounced in that seizure of the nut to the bolt can occur by galling when the steel bolt and nut assembly is made at ambient temperature. In order to alleviate this problem, it has been the custom to apply a lubricant or anti-seize compound to the threaded portion of the securing member prior to engaging the securing member with the nut or other fastening element. The commonly employed lubricants or anti-seize compositions include greases, oils, metallic compounds and graphite. Unfortunately, however, some of the above-mentioned materials are not entirely satisfactory for use at elevated temperatures and those which are suitable are relatively expensive and add to the cost of fabrication.

We have discovered an antiseize material, that is, a material which prevents seizure and/or galling of the fastening element to the securing member which material is inexpensive, easy to apply and which maintains its property under severe conditions of elevated temperatures over extended periods of time.

It is, therefore, an object of the present invention to provide a new antiseize material.

Another object is to provide a process for treating metallic securing assemblies, of the type wherein a metallic securing member threadably engages a fastening element, to prevent seizure of the fastening element to the securing member.

A further object is to provide a process for treating threaded steel members prior to engaging the nut or other fastening element thereto to prevent seizing of the nut to the threaded steel member. These and other objects will be apparent from the following description.

The antiseize material of the present invention is a chrysotile asbestos, preferably a chrysotile asbestos which has been comminuted into a fine powder and a carrier therefor, and which has been treated to remove gangue materials and other impurities. As is known, chrysotile asbestos generally occurs in mineral deposits in the form of closely packed fibers. The process of separating the fibers from the asbestos ore in which they occur generally comprises a series of crushing and winnowing operations whereby the fibrous rock is subjected to mechanical pressure and shock, and during these operations the fiber is carried away by air currents and the associated rock is discarded.

For some commercial operations where the purity of the product is not of substantial significance, the above procedure for producing a chrysotile asbestos has been found to be generally satisfactory. In many important commercial operations, as well as in the present invention, however, it is preferred that the asbestos material have a high degree of purity, that is, that the final product contain little or no gangue or other impurities, and moreover, that the fiber bundles be separated into individual fibrils from each other.

Several techniques have been proposed to chemically disperse the asbestos fibrils and thus obtain more complete separation of individual fibrils from each other and from gangue and other impurities. Such chemical dispersion techniques are described in U.S. Pats. 1,907,616; 2,661,287; 2,626,213 and 3,062,701, for example.

A particularly suitable and preferred procedure for preparing asbestos dispersions is described in U.S. Pat. 3,297,516. Generally, the process described therein comprises contacting an aqueous slurry of chrysotile asbestos with a metal aluminate such as potassium aluminate, calcium aluminate or barium aluminate. To the slurry is added a monobasic acid, such as, acetic acid, formic acid, hydrochloric acid, or nitrous acid until the pH of the resulting aqueous slurry is from about 4.0 to about 6.0. As a result there is formed a highly charged, strongly adsorbable, polymolecular colloid of material consisting of aluminum hydroxide or hydrated aluminum oxides. The slurry is thereafter subjected to high speed shearing forces to provide asbestos dispersions which are useful as a source of finely divided asbestos. Purification, i.e. separation of gangue and other impurities can thereafter be easily effected by known gravity methods.

The chrysotile asbestos antiseize material can be applied to the threaded portion of the securing element in any convenient form such as in the form of powders, dispersions, suspensions and the like. A particularly convenient procedure is to utilize the chrysotile asbestos in the form of a paste containing the chrysotile asbestos in finely divided, pulverized form. Thus, when employing the above-mentioned prior art procedures for preparing dispersions of the asbestos material, the aqueous dispersion can be filtered thereby forming a "cake" of the asbestos material. A liquid carrier, such as a paraffinic oil preferably mineral oil, alkyl glycols, water and the like can then be added to form a paste-like consistency to the mass. In general, the chrysotile asbestos comprises from about 10 to about 60 percent by weight of the weight of the composition, preferably 15 to 30 percent by weight. Thus the carrier can comprise 40 to 90% and preferably 85 to 70% carrier.

In some cases the presence of alkali and/or chloride contaminants in the asbestos can have a detrimental effect

A 13648 [redacted]

Published by AsbestosClaims.Law
asbestosclaims.law/library/15382/17

on the material to be serviced. For example, the presence of significant quantities of chloride in the asbestos could cause stress-corrosion cracking of austenitic stainless steels and the presence of alkali can have a detrimental affect on iron fasteners. For this reason, it is preferred that these contaminants be removed from the asbestos. A convenient and effective procedure for removing alkali and chloride from asbestos involves diluting the asbestos so as to obtain above 2% solids by weight asbestos in distilled water or deionized water. In this manner, the contaminants diffuse from the surface of the asbestos into the bulk water. Thereafter the bulk water is separated from asbestos by a conventional filtration procedure.

The securing assemblies to which the present invention is directed are those which normally are effected by changes in temperature, pressure, time and other variables which cause "seizing" of the assembly, e.g. the seizing of the nut to a bolt.

Merely as illustrative, the antiseize material can be effectively employed in connection with securing assemblies fabricated from iron, steel, stainless steel, nickel-base alloys, cobalt-base alloys and complex super-strength stainless steel alloys and the like.

The method for applying the chrysotile asbestos material to the securing assembly can be varied and depends in part on the form in which the asbestos is to be applied. Where the chrysotile asbestos is the sole essential material i.e. without a carrier, such as finely pulverized chrysotile material in powder form, then a convenient procedure for application is to spray the asbestos material into the threaded portion of the securing member. However, this procedure is not preferred because of the lack of adherence of the asbestos material to the securing member. This disadvantage can be minimized however by first coating the threaded member with an adhesive prior to application of the chrysotile asbestos.

When the chrysotile asbestos is employed in the form of a paste, the material to be serviced can be immersed in the paste to the extent of the threaded portion or alternatively the paste can be applied by rubbing the paste onto the surface of the threaded portion of the securing member. It will, of course, be understood that the antiseize material can also be applied to the threaded portion of the fastening element in lieu of the above or in addition to the above that a variety of techniques can be employed for this purpose.

The invention will be more fully understood by reference to the following specific examples. These examples are merely illustrative of the practice of this invention and are not intended to limit the invention in any manner other than as defined in the appended claims.

EXAMPLE 1

The chrysotile asbestos employed in this example was in the form of a heavy paste containing high-purity, resin-grade, short fiber white asbestos sold by the Mining & Metals Division of Union Carbide Corporation. The paste contained 19.3% chrysotile asbestos and 80.7% mineral oil.

In this example, the antiseize composition was tested in connection with one-half inch diameter by two-inch long, hex-head, coarse-thread, machine bolts of type 304 stainless steel. Two nuts and two flat washers of the type 304 stainless steel were placed on the threaded portion of each bolt. The antiseize material was applied by hand to the threads of the bolt, and a nut was screwed on the bolt. The threads were again recoated, the washers were coated individually and placed on the bolt and the second nut thereafter screwed on the bolt. The nuts were thereafter tightened onto the bolt with a torque wrench having a dial indicator reading of zero to ±600 in.-lbs. (50 ft.-lbs.) and were preloaded to 30 ft.-lbs. or 360 in.-lbs. torque preload. The nuts were loosened and a measurement taken as to the amount of breaking torque required to loosen the nuts. The nuts were again tightened to 360 in.-lbs. preload a second time and again loosened. The nuts were tightened to 360 in.-lbs. torque preload a third time and thereafter exposed to a temperature of 1200° F. for 793 hours and the breaking torque after exposure was again measured. The results are indicated in Table I.

EXAMPLE 2

The procedure of Example 1 was repeated and the results indicated in Table I.

EXAMPLES 3 AND 4

The procedure of Example 1 was repeated, except that the antiseize material was pulverized chrysotile asbestos which was present in an amount of 27.1% in water and the tests were conducted on two stainless steel bolts.

The results of the foregoing Examples are indicated in Table I and are compared with a control in which no antiseize material was employed.

TABLE I.—STAINLESS STEEL BOLT ANTISEIZE TESTS AT 1,200° F. FOR 793 HOURS

[½" dia. type 304 bolts with 2 nuts and 2 flat washers, lubricant in threads and between washers (30 ft.-lbs. or 360 in.-lbs. torque preload)]

Example No.	Antiseize material	Breaking torque immediately after preloading		Breaking torque after exposure	Condition of material and bolt after exposure
		1st preload	2nd preload		
1	19.3% fluffy asbestos in mineral oil.	310	360	425	Front nuts finger-loose after breaking, back nuts fairly loose. No galling. Soft, fluffy white coating, very good lubricating "feel."
2	Same as Example 1	370	390	400	Same as Example 1.
3	27.1% pulverized asbestos in water.	360	410	800	Same as Examples 1 and 2 except better distribution and retention of coating in threads.
4	Same as Example 3	380	430	825	Same as Example 3.
Control	None	290	300	>600	Galling occurred.

What is claimed is:

1. A method of treating metallic securing assemblies of the type wherein a metallic securing member threadably engages a fastening element to prevent seizure of the fastening element to the securing member at the site of threadable engagement which comprises applying to the portion of the securing member to be threadably engaged with said fastening element a chrysotile asbestos.

2. A method according to claim 1 wherein said chrysotile asbestos is applied in the form of a paste comprising 15 to 30% chrysotile asbestos and 85 to 70° of a carrier therefor.

3. A method according to claim 1 wherein said chrysotile asbestos is applied in the form of a paste comprising 10 to 60% chrysotile asbestos and 40 to 90% of a carrier therefor.

4. A method according to the claim 2 wherein said carrier is water.

5. A method according to claim 2 wherein said carrier is an alkyl glycol.

6. A method according to claim 1 wherein said securing assembly is fabricated from stainless steel.

7. A method according to claim 1 wherein said

A 13649

metallic securing member is a steel bolt and wherein said fastening element is a stainless steel nut.

8. A method according to claim 2 wherein said chrysotile asbestos is a finely divided, pulverized chrysotile asbestos.

9. A metallic securing assembly comprising a securing member in threadable engagement with a fastening element and a chrysotile asbestos disposed at the site of said threadable engagement.

10. A metallic securing assembly according to claim 9 wherein said securing member and fastening element is fabricated from stainless steel.

11. A metallic securing assembly according to claim

10 wherein said securing member is a bolt and said fastening element is a nut.

References Cited

UNITED STATES PATENTS

2,419,252	4/1947	Bychinsky et al.	117—127 X
3,061,455	10/1962	Anthony	117—127 X

EDWARD G. WHITBY, Primary Examiner

U.S. Cl. X.R.

85—1 C; 117—121, 135.1, 169 R; 252—14, 28

[redacted]

A 10850

United States Patent Office 3,838,085 Patented Sept. 24, 1974

3,838,085

PIGMENTED ASBESTOS LATEX EMULSION PAINT COMPOSITION

John L. Myers, Lewiston, N.Y., and Richard W. Lasher, Palos Verdes Peninsula, and Russell D. James, La Mirada, Calif., assignors to Union Carbide Corporation, New York, N.Y.

Continuation-in-part of abandoned application Ser. No. 34,796, May 5, 1970. This application Oct. 24, 1972, Ser. No. 300,193

Int. Cl. C08f 45/24

U.S. Cl. 260—29.6 R 16 Claims

ABSTRACT OF THE DISCLOSURE

Premium latex paints are disclosed exhibiting superior opacity and brightness characteristics, including dispersed and liberated short chrysotile asbestos fibers having anionic pigment particles electrostatically attached at discrete points along the length of the fibers.

This application is a continuation-in-part of copending application Ser. No. 34,796, filed May 5, 1970, now abandoned.

The present invention relates to pigment dispersions and coating compositions and, more particularly, to latex paints including a dispersion of pigmented asbestos fibers.

High quality finish paints include hiding pigments such as rutile titanium dioxide (TiO_2) which have a high refractive index (2.7) compared to the other ingredients in the system. Opacity, or hide, is a function of the difference in refractive index between the TiO_2 and the pigment binder (1.5). The different refractive indices cause the incident light to be bent through a succeeding series of angles within the coating by alternately striking pigment binder, then titanium dioxide. The ultimate result is to reflect the incident light ray.

To optimize this mechanism within a coating system, the titanium dioxide must be thoroughly dispersed. Presently, high speed dissolvers are employed to impart extremely high rates of shear to disperse the titanium dioxide. Surface active agents aid the process by lowering the surface tension of the liquid medium in which the pigments are dispersed, and help keep the pigments separated once the shear is stopped. However, it has not been possible in practice to completely disperse the pigment particles which tend to agglomerate and reduce the optical efficiency of the paint film.

In accordance with the present invention, improved pigment dispersions and paint compositions are prepared by dispersing and firmly holding the pigment particles along the length of liberated, i.e. discrete, highly cationic, colloidal, short fiber, high purity asbestos fibers. When aqueous pigment dispersions containing such pigmented asbestos are incorporated into paints, the resulting film exhibits an increased opacity and has several other unexpected effects.

Even though the asbestos itself is a gray dull material and has a fairly low brightness, unexpectedly the paints incorporating the aqueous pigment dispersions according to the invention have very high brightness levels. It has further been surprisingly discovered that although asbestos usually occurs as lumps which would prevent the dispersability and a fine grind, a very fine finished aqueous latex paint having dispersed solids of a grind or fineness below 2 mils, can readily be manufactured from the aqueous pigment dispersions containing the pigmented asbestos fibrils in accordance with the invention.

The pigmented asbestos of the invention in addition provides improved structural strength to the film and also can decrease or eliminate the necessity for the use of biodegradable thickeners such as cellulose ethers. Furthermore, since the pigmented asbestos is a less costly product than pure pigment, the cost of manufacture of the paint can be significantly reduced.

Pat. No. 3,328,238 to Knowles et al. discloses stable suspensions of organic or inorganic fibers, including asbestos fibers, in a hydrocarbon vehicle, for use as propellant suspensions, agricultural compositions, oil base drilling fluids, and oil base paints. In the latter application the microfibers act as a suspending matrix for the pigments in the paint, forming a fibre thickened vehicle or gel in which the pigment solids are dispersed. However, this patent bears no relation to and does not suggest the aqueous latex emulsion paint composition of the present invention in which the high purity chrysotile asbestos fibers having certain physical characteristics are predispersed in water to develop a cationic charge so as to electrostatically bond anionic pigments to the asbestos fibers, to form the pigmented asbestos of the invention, as described in detail below.

The above and many other attendant advantages of the invention will become apparent as the invention becomes better understood by reference to the following detailed description when considered in conjunction with the accompanying drawings wherein:

FIG. 1 is an illustration of the appearance of dry processed Calidria fibers, one form of high purity crysotile asbestos fibers, at 20,000 magnification;

FIG. 2 is an illustration of the appearance of wet processed Calidria fibers;

FIG. 3 is a flow chart illustrating alternative processes for forming pigment dispersion;

FIG. 4 is an illustration of pigmented liberated fibers of FIG. 2; and

FIG. 5 is a graph illustrating the relationship between the solids content of refined asbestos filter cake and degree of pigment dispersion in terms of National Standard (N.S.) Grind Numbers.

It has been discovered in accordance with the invention that the above advantages are obtainable with particular forms of asbestos having certain surface area, lengths, fiber availability, and very high cationic charge density. The high charge density and liberated form of the fibers allow the fibers to electrostatically bond firmly to anionic pigment which satisfies the charge to form a highly pigmented fibrous product. By the term "liberated" fibers or fibrils is meant that such fibers are in the form of discrete fibers or fibrils, rather than in the form of fibril bundles. Without the electrostatic bonding of the pigments to the fibers to satisfy the cationic charge on the fibers, the available cationic charge on the fibrils reacts with and agglomerates anionic latex particles. Without the cationic fibers, the anionic pigments will tend to agglomerate, reducing optical efficiency. When these materials are combined according to the invention, the pigment is uniformly distributed along the length of the fibers so that the final product resembles and performs like a fibrous pigment. The uniform distribution of the pigmented fibers results in a very high optical efficiency and therefore less hiding pigment is needed to obtain a given opacity.

Pigment dispersions in accordance with the invention incorporate a particular type of high purity chrysotile asbestos. Generally, chrysotile asbestos has a low index of refraction of about 1.51 to 1.55, is the softest and most flexible of the several types of asbestos. When dispersed in water it exhibits a positive or cationic surface charge and a very high tensile strength. Chrysotile asbestos occurs only in serpentine, a fine grained rock composed entirely of hydrous magnesium silicate minerals similar to chrysotile in composition. Most deposits of serpentine contain chrysotile in cross-fiber veins, and the ore typically contains only 6 to 10 percent fiber of random lengths

A 13651

which are tightly bonded together in a parallel configuration.

The unique materials according to the invention bear little resemblance to other serpentine bodies since most of the mass of fibers are highly sheared and pulverized and consist of soft, friable sheets and clumps of asbestos fiber. In contrast to the cross-fiber arrangement of conventional Canadian ores, the high purity chrysotile asbestos material, one form of which is marketed as Calidria asbestos fibers, and is preferred for use in the present invention, is obtained from a deposit near Coalinga, Calif., occurs as a swirling mesh of disoriented fibers.

Conventional asbestos processing methods include blasting, crushing and grinding, and air classifying. Even with the use of the very best dry method of processing high purity chrysotile asbestos ore, fiber bundles are still very much in evidence as shown in FIG. 1. The high purity chrysotile asbestos utilized in the present invention is preferably refined in accordance with a hydraulic beneficiation process to provide substantially separated fibrils 10 as shown in FIG. 2. In the hydraulic beneficiation process, the ore is treated by wet grinding and screening to separate rock from asbestos fiber, flakes and clumps. The asbestos is then subjected to wet mechanical and/or chemical treatment to liberate the fiber, that is, to separate the fibers into discrete fibers, and separate out occluded non-asbestos minerals to form standard grade product. High purity product is obtained by further wet grinding and centrifugal processing of the standard grade product. This process results in separated, individual or discrete fibers of high purity, high liberation and uniform particle size. Thus, this asbestos is different from any other asbestos product available. The physical properties of average Canadian, standard grade Calidria and high purity Calidria asbestos are provided in the following table.

PHYSICAL PROPERTIES OF CHRYSOTILE ASBESTOS

Property	Average Canadian	Calidria products: Standard grade	Calidria products: High purity
Surface area, m.²/g.	10–30	50–60	60–80
Reflectance, percent	64–70	62–72	72–76
Magnetite, percent	3–6	2.0	<0.80

Specific surface area is calculated from adsorption data using the BET (Brunauer, Emmet, Teller) method as described in Brunauer, "The Adsorption af Gases and Vapors," Princeton University Press (1945).

Magnetite content is measured by a permeametric device patterned after ASTM standard method D–1118–57, which has been improved with respect to sensitivity to measure a limit of detection of 0.005% magnetite.

Reflectance is measured on a sample prepared according to TAPPI (Technical Association of the Pulp and Paper Industry) standard T–452–m–58 and is reported as percent of ultimate reflectance based on magnesium oxide as the standard of 100% reflectance.

The significantly greater purity of the high purity chrysotile asbestos essential in this invention is demonstrated by its improved reflectance of at least 72% and its low magnetite content of less than 0.8% magnetite. The wet processing procedure gives rise to high purity asbestos fibers that are essentially grit-free and of high brightness. The reduced magnetite content of the pure flake product is also a measure of absence of gray appearance that has been characteristic of prior asbestos products. The reduced grayness and absence of black specks is essential in the preparation of premium quality finished paints.

The individual asbestos fibers are in the form of slightly-curved, short tubes having an external diameter of about 260 A. and an internal diameter of about 110 A. The length of the fiber varies from about 100 to 1,000 times the diameter and the average L/D ratio is about 200. Thus, the average fiber length is about 5 micron and it is estimated that there are about 10^{14} fibrils in one gram of the high purity chrysotile asbestos.

The virtue of their small diameters and high aspect ratio, the high purity chrysotile, asbestos fibrils form colloidal suspensions when suspended in water and behave according to the classical electrokinetic rules of hydrophobic colloids. That is, the fibrils develop a surface charge when suspended in aqueous solution as the result of adsorption of potential determining ions from the suspnding medium. The potential determining ions are mainly hydrogen, and therefore, the fibers display a positive charge in the basic pH range. Thus, the term "cationic" asbestos as employed herein is intended to denote asbestos or asbestos fibers which exhibit a cationic charge when dispersed in water under the pH conditions, usually about 4 to about 9.5, generally used in the paint industry. Electrostatic attraction, however, is just one of the factors that influence the effectiveness of the fibers in cofloccing pigment particles. Collision and coagulation rate in suspension are determined by the collision radius which varies as the longest dimension of the particle while diffusion constant varies as the main particle dimension. The net result for the rod-like, high purity chrysotile asbestos particles is a very large effective collision radius and a large diffusion constant. Furthermore, the high surface area of the high purity asbestos fibers, ranging from about 60 to 80 meters²/gram, in combination with the cationic charge provides a very high cationic charged density for attracting and firmly holding the pigment particles.

The high purity chrysotile asbestos can be provided in several forms, particularly useful in forming the pigment dispersion in accordance with the invention. The final form of the fiber in the pigment dispersion is preferably a totally liberated, colloidal form. This is usually achieved with the particular high purity, short fiber chrysotile asbestos of interest which has an ultimate fiber yield of at least 85%, e.g. 85–95%. Canadian chrysotile asbestos fibers, as represented by Canadian 6–D–20 (see Example IX) is only liberated to an extent of about 25–40% ultimate fiber yield under the same conditions.

Ultimate fiber yield is determined by pulping 3 grams asbestos in 250 ml. of tap water at high speed in a Waring Blender for 3 minutes. The pulp is washed into a beaker to a final volume of 300 ml. The pulp is dispersed, decanted, flocculated, dried and weighed. Percent ultimate fiber yield is the supernate chrysotile asbestos filter cake weight times 3 divided by the total weight of the two cakes times 100.

The filter cake of liberated asbestos fibers in accordance with this invention is a lightly compacted, essentially non-agglomerated product which is readily redispersible in water with conventional mixers to form an aqueous dispersion containing liberated fibers.

In the first step of making a high quality paint formulation in accordance with the invention, a dispersion of pigments is prepared. The pigment dispersion can contain varying amounts of the pigmented asbestos usually ranging from 1% to 25%, preferably 5% to 10%, of the total solids of the dispersion, depending on the water demand of the various components of the system, the properties desired for the final paint composition and properties desired for the final paint film. The unpigmented high purity chrysotile asbestos fibers have a water demand of about 480% while the pigmented fibers have a lower water demand depending on the quantity and type of pigment.

The demand for pigment in terms of cationic charge is preferably completely or totally satisfied by anionic pigments. The high purity chrysotile asbestos fibers develop a total positive charge which must be completely balanced by combining with a total negative charge which is furnished by the anionic pigment, resulting in electrostatic bonding of anionic pigment along the length of its fibers. It has been found that in order to completely satisfy the cationic charge on the asbestos fibrils, it is necessary to employ a ratio of at least nine times anionic pigment to asbestos, by weight. Thus, in totally liberated or discrete form, the asbestos fibers or fibrils can cofloc or satisfy

A 13652

about 9 to 10 times the weight thereof with anionic pigment.

The fibers may be totally pigmented with a primary hiding pigment having high efficiency and providing opacity such as rutile titanium dioxide. Anatase titanium dioxide may be used where chalking is desired. Other anionic hiding pigments comprise zinc sulfide, zinc oxide, basic silicate of white lead, lithopane, iron oxide or antimony oxide. Any combination of these hiding pigments may be utilized. In another procedure in accordance with the invention to be discussed below, the fibers may be pigmented with a mixture of anionic hiding pigments or a mixture of anionic hiding and extender pigments. Typical extender pigments and the amounts in percent by weight in which they may be present are provided below. These extender pigments may be combined as desired for a particular end result.

1. Calcium carbonate (whiting) 0 to 25%
2. Hydrated aluminum silicate (clay) 0 to 25%
3. Magnesium silicate (talc) 0 to 8.5%
4. Silicon dioxide and calcium silicate (silicas) 0 to 4.5%
5. Potassium aluminum silicate (micas) 0 to 6.5%
6. Other pigments including barium sulfide, bentonite, magnesium aluminum silicate and various organic and inorganic and crystalline pigments.

The hiding pigment such as titanium dioxide, and the extender pigments such as clay and calcium carbonate, exhibit an anionic or negative charge when dispersed in water as result of attachment of hydroxyl groups to the pigment, and hence are termed "anionic" pigments herein.

Total pigment present in the paint composition of the invention can range from about 4 to about 65% by weight. Anionic hiding pigments are present in an amount generally of about 4% to 25% by weight, or higher. The preferred hiding pigment due to its efficiency in providing opacity is rutile titanium dioxide. Other hiding pigments noted above may be present to replace a part or all of the rutile titanium dioxide.

Referring now to FIG. 3, several processes for forming pigment dispersion containing coflocced pigmented asbestos are illustrated. In the pellet or open fiber process (I), a dilute liberated asbestos slurry such as a slurry containing 2.5% asbestos is blended with an anionic hiding pigment such as rutile titanium dioxide. Oppositely charged asbestos fibers and titania particles are attracted and bond to each other to form a coflocced product as illustrated in FIG. 4 which shows the fibrils **10** having particles of titania **12** electrostatically attached along the length of the fibers to form a predispersed product. In the pellet, and open fiber process, the ratios of materials are adjusted to form a product containing from 1 to 90% titania, suitably about 35% titania, though the asbestos is capable of holding up to 9 times or more, e.g. 9 to 10 times, its own weight of pigment. The coflocced slurry is dewatered, extruded into pellets and dried in a rotary dryer. The dried pellets can be milled to form an open fiber form of the product.

The paint formulator may predisperse the pellets or open fiber in water with a high shear mixer to form a liberated slurry of the partially titanated asbestos. The remaining pigments are then added, continuing the high shear mixing to form the final pigment dispersion. The separate dispersion in water with high shear mixing better assures complete liberation of the fibers, to form a paint having a fine grind. Alternately, the remaining pigments in water can be added directly to the pellet or open fiber, and mixed with high shear to form the pigment dispersion. The dispersion of the high purity chrysotile asbestos is materially aided by reducing the pH of the slurry to the acid range, preferably from about 4–5. An electrostatic condition in the slurry under these conditions prevents the fibers from reagglomerating.

In the filter cake process, (II), the dilute liberated asbestos slurry is dewatered in a vacuum frame press to form a filter cake containing 40–60% asbestos fiber which may be optionally dried with tumbling in a rotary drier to a homogeneous product having a solids content of 80–90% asbestos. Again, the pigment dispersion can be formed by adding the total pigments at one time to the dispersion of fibers, with blending or separately predispersing the hiding pigment such as rutile titania before adding the remaining pigments and blending to form the pigment dispersion.

A series of experiments were run to determine the critical percent fiber that could be provided in a reduced water content chrysotile asbestos filter cake that is readily dispersible with conventional mixers available to most paint processors, rather than the high shear and high horsepower mixers necessary to completely disperse the pretitanated pellets. Standard interior latex paints were prepared according to the formulation of Example 4 with each of these filter cakes. The results are tabulated in the following table and FIG. 5.

TABLE II.—LATEX PAINT CONTAINING FILTER CAKE

Filter Cake— Asbestos Weight Percent	Latex Paint of Example 4—National Standard Grind No.
41	6
55	5.6
75	4.5
91	4.5
96	4

Wrinkling was evident at about 91% solids level in the filter cake, and above, indicating incomplete fiber liberation and therefore the presence of available cationic charge which causes coagulation of the anionic latex.

Unexpectedly, the filter cake can be dewatered to a level as high as about 91% by weight of asbestos and still maintain an adequate grind of 4.5, corresponding to less than 2 mils, in the resulting latex paint, indicating fairly good liberation and noncompaction of the fibers into bundles. It is however, preferable to maintain the asbestos content of the filter cake from about 80 to 90% to provide finer finish paint films. The 80 to 90% asbestos filter cake product affords substantial absence of wrinkling as well as adequate grind of less than 2 mils for the latex paint in which such filter cake is incorporated, and is otherwise a very desirable commercial form of asbestos since the water content thereof is sufficiently low to minimize shipping costs and it is a form readily available for dispersion.

The dispersion containing the dispersed pigmented asbestos is incorporated into a latex paint which is defined as a paint in which water is the principal diluent. The nonvolatile portion of the paint is between 30 and 80% while the pigment volume concentration (PVC):

$$\frac{\text{pigment volume}}{\text{pigment volume}+\text{vehicle volume}}\times 100$$

is between about 15% and 80%. The paint may optionally also contain binders, solvents, thickeners, surfactants and various other additives. Exemplary materials for each component with a suggested percentage basis based on the total weight of the paint are provided below. These ingredients are understood to be exemplary and are not intended to any way limit the invention, it being understood that alternate materials can readily be substituted for those suggested.

A general procedure for formulating paint compositions according to the invention is to first charge all liquid ingredients including optional thickeners, and optionally including a portion of the vehicle, especially in the case of modifier vehicles. The charge is thoroughly mixed and the solids namely, the anionic pigment and cationic asbestos fibers, are then added under high shear dispersion. In the case of anionically charged vehicles, such as anionic resins, the presence of the cationically charged asbestos renders it necessary for prepigmentization of the

Union Carbide trial exhibit UC-106: Five Union Carbide U.S. Patents on Asbestos Uses: Filled Polymers, Fire-Figh… Published by AsbestosClaims.Law
ACL Doc 15382 · Page 22 of 30 asbestosclaims.law/library/15382/22

asbestos to completely satisfy this cationic charge, before addition of the anionic vehicle; otherwise, coagulation of the anionic resin will occur as result of the combination of anionic resin with unsatisfied cationic charge on the asbestos. Nonionic vehicles, e.g. nonionic resins, can be added at any stage of the manufacture.

The diluent concentration is preferably maintained between about 20 to 70%. While water is the primary and predominant diluent in a latex paint system, solvents for modifying resin vehicle may also be present. The percentage range also includes the water present in such vehicle portion.

Substantial thickening of the paint is provided by the fairly high water demand of the asbestos. In some cases, secondary thickeners need not be present. However, in most cases, the viscosity of the paint can be adjusted to the desired range of 60 to 125 K.U. preferably 80 to 105 K.U., by including 0 to about 4% of conventional thickeners such as water soluble cellulose derivatives, e.g. cellulose ethers or esters, for example, hydroxyethyl cellulose, methyl cellulose, and carboxymethyl cellulose. Other types of materials can also function as thickeners such as carboxylated polyacrylic acids, sodium alginate, bentonite clays, a polymethylvinyl ether reaction product with maleic anhydride, and polysaccharides. The expression "K.U." refers to Krebs units, a measure of viscosity which is conventionally used in the paint industry, and is determined with the Krebs-Stormer viscometer, as described in the brochure of the Arthur Thomas, Co., Philadelphia, Pa., "Directions for Use of Stormer Viscosimeter," published 1948.

Surface active agents which function as surfactants and dispersants can be present in the range of about 0.1% to 4% by weight of this composition. These ingredients wet the surfaces of the particles and stabilize the emulsion or colloidal system. Usually only anionic and nonionic compounds are utilized in latex paints and preferably a mixture of these types of surfactants is utilized. Many diverse types of surfactants which are commonly used in the formulation of latex paints are suitable for use in forming the pigmented asbestos latex paints in accordance with the invention.

Exemplary anionic surfactants are saponified fats, sulfonated materials such as fatty acid esters, monovalent alcohol esters of fatty acids. fatty acid amides, fatty acid nitriles, fatty aldehydes, secondary alcohols, or aromatic hydrocarbons. Other suitable anionic surfactants are alkali sulfonates of alcohols having 6 or more carbon atoms, aminopolycarboxylic acids and the condensation products of fatty acid chlorides and amines.

There are fewer non-ionic compounds commercially available. Exemplary non-ionic surfactants are saponines and their derivatives, the condensation products of ethylene oxide with fatty acids and their derivatives or with phenolic compounds having a side chain.

Coalescing agents can be provided in an amount of 0 to 4.5% as needed. Coalescing agents aid in film formation during the drying cycle. They are solvents for the vehicle and eventually evaporate from the paint film. Typical coalescing agents include plasticizers such as dibutyl phthalate, glycols like hexylene glycol, glycol-ethers, and certain alcohols.

Freeze-thaw stability is an important property for paints stored in cold climates. Glycols such as ethylene glycol, diethylene glycol and propylene glycol are added in an amount of 0 to 4.5% to insure freeze-thaw stability.

Latex emulsions, e.g. an anionic, nonionic or cationic latex, and various modifiers therefore, can be provided in an amount providing about 5% to 50%, preferably about 5% to 25%, by weight of resin solids in the paint composition. Latex emulsions can be comprised of many polymer types, and commercially available emulsions contain 30% to 70% by weight resin solids in the form of nonvolatile polymer. The polymer generally employed according to the invention contains an ethylenically unsaturated polymerizable vinyl group. The polymer functions to bind the pigment particles together and to bind the paint film to the substrate. Generic types of suitable latex emulsions and polymers are listed below:

1. Polyvinyl acetate homopolymer latexes.

2. Vinyl Acetate—acrylic copolymer latexes. The acrylic portion includes but is not limited to ethyl acrylate, isobutyl acrylate, methyl methacrylate, N-butyl acrylate, methacrylic acid, N-methylol acrylamide, acrylonitrile, 2-ethyl hexyl acrylate, and acrylic acid. Furthermore, these ctpolymers may contain itaconic acid, styrene, butadiene, ethylene, vinyl chloride, maleates, and fumarates. Specific examples of such polymers are the copolymer of vinyl acetate and butyl acrylate, vinyl acetate and 2-ethylhexyl acrylate, vinyl acetate and dibutyl maleate.

3. Acrylate Latexes—The acrylate latexes may contain any combination of acrylate and acrylic monomers noted above in vinyl acetate-acrylic latexes, except for vinyl acetate. Specific examples of such polymers are the copolymer of ethyl acrylate, methyl methacrylate and methacrylic acid, and the copolymer of butyl acrylate, methyl methacrylate and acrylic acid.

4. Other latexes include polymers of styrene-butadiene, styrene-acrylic, acrylonitrile-butadiene rubber, butadiene rubber, and ethylene-vinyl acetate, vinylidene-chloride, and acrylate-vinyl chloride polymers.

It will be understood that the proportions of comonomers in the above described copolymers can be varied as desired and as well understood in the art, to obtain the desired properties. Thus, for example in the copolymer of vinyl acetate and butyl acrylate the monomer proportions can range from 90 to 75% vinyl acetate monomer and 10 to 25% butyl acrylate monomer; and in the copolymer of ethyl acrylate, methyl methacrylate and methacrylic acid, the proportions of monomers can range from 40 to 70% ethyl acrylate, 20 to 35% methyl methacrylate and 0.5 to 3% methacrylic acid.

Latexes containing combinations of the above resins can also be employed, such as a combination of vinyl acetate homopolymer and copolymer of vinyl acetate and butyl acrylate.

The resins in the above latexes in the presence of anionic surfactants generally achieve an anionic charge. This is due to the polymerization of the monomers to form the resins, in the presence of such surfactants carrying an anionic charge. Polymerization can also be achieved in the presence of nonionic and cationic surfactants, in which case the resulting resins are either nonionic or cationic in nature. However, because of the cationic charge of the chrysotile asbestos fibers, the anionic latexes generally employed to the major extent in latex paints, must be added to the dispersion of the chrysotile asbestos fibers after addition thereto of the anionic pigment in order to completely satisfy the cationic charge of the fibers with the anionic charge of the pigment, prior to addition of the anionic latex, to avoid coagulation, as noted above.

Any of the above latexes may be modified with organic solvent based binders or oils which may be of the drying or nondrying type. These modifiers in turn may be emulsified. Modifiers may comprise from 0 up to 70% of the vehicle solids in a given paint in which water is the principle diluent. Suitable modifiers are the oils such as linseed oil, tung oil, safflower oil, tall oil rosins or tall oil esters. Resin modifiers comprise alkyd resins, epoxy resins, vinyl resins, acrylic resins, silicone resins, phenolic resins, ester gums and cellulose resins.

Various miscellaneous ingredients may be present in an amount of 0% to 4% by weight. Included in this category are defoamers which may or may not contain silicones and fungicides, of the mercuric and non-mercuric types. Driers for the solvent based modifier such as cobalt, zinc or magnesium naphthenates or phthalates may also be provided when needed. Other various materials

A 13654

may be incorporated for special purposes as are well known in the art.

Generally the paint composition of the invention includes, in addition to the dispersion of the pigmented asbestos and latex, additional optional components, particularly thickener, surfactant, e.g. anionic surfactant and coalescing agent.

A series of paint formulations were prepared by first charging in order, water, thickener, surfactant, fungicide, freeze-thaw additive, coalescing agent, and about ½ of the defoamer, and mixing for 5 minutes at low speed. Thereafter, the TiO_2 was added and dispersed until a desired dispersion was achieved. Mixing speed was increased. The remaining pigments, including calcium carbonate, clay and the high purity chrysotile asbestos fibers, were then added and mixed at high speed to form a pigment-asbestos fiber dispersion. The latex and remainder of the defoamer were then added to the pigment-asbestos fiber dispersion at low speed. Agitation should be continuous and each ingredient dispersed before the next is added.

The chemical identification of each ingredient by type, formula and function is provided wherever possible. The asbestos utilized in each case, except for Example 9, was high purity, short fiber chrysotile asbestos in the form of Calidria asbestos as either dispersed unpigmented filter cake or in pretitanated pellet form, as indicated. The ingredients utilized in the formulations are provided in the following table, and the examples follow thereafter.

TABLE III

Function	Material	Generic type
Solvent	Water	H_2O.
Thickener	Bentone LT	Organically modified bentonite.
Anionic surfactant	TAMOL 731	Sodium salt of diisobutylene maleic anhydride.
Do	VICTAWET 35B	Sodium octyl phosphate.
Nonionic surfactant.	ADVAWET 33	Polyglycol ester.
Freeze-thaw	Ethylene glycol	
Coalescent	Butyl carbitol acetate.	Monoether of diethylene glycol.
Defoamer	NOPCO NXZ	0.1% Si.
Fungicide	CMP acetate	Chloromethoxy-acetoxy mercuripropane.
Hiding pigment	Ti pure R-960	TiO_2.
Extender pigment	ASP 170 clay	Kaolin clay.
Do	VICRON 25-11	Calcium carbonate.
Extender pigment, asbestos	CG 100	High purity chrysotile.
Extender pigment, titanated asbestos.	CG 135	High purity chrysotile, plus 35% TiO_2.
Extender pigment, filter cake.	CG 100	40 to 50% solids.
Extender pigment, titanated filter cake.	CG 135	40 to 55% solids.
Solvent	Water	H_2O.
Defoamers	NOPCO NXZ	
Latex emulsion	NAT-1 (55%)	Copolymer of vinyl acetate and butyl acrylate (anionic).
Do	UCAR-130 (58%)	Vinyl acetate homopolymer (nonionic).
Do	UCAR-370 (46%)	Acrylic emulsion containing copolymer of ethyl acrylate, methyl methacrylate, and methacrylic acid (anionic).
0.1 modifier	PVO-44 (65%)	Bodied safflower emulsion.
Epoxy modifier	Polytet 611 Q	Epoxy ester emulsion.
Thickener	Cellosize QP-4004	A hydroxy ethyl cellulose.

EXAMPLE I

Material:	Pounds
Water	225
Bentone LT	5.5
TAMOL 731—25% Active	3
VICTAWET 35B	5.7
ADVAWET 33	4
Ethylene Glycol	15
Butyl Carbitol Acetate	15
NOPCO NXZ	2
CMP Acetate	0.5
Ti Pure R-960	242.5
ASP 170 Clay	100
VICRON 25-11	144.7
Water	151
NOPCO NXZ	2
NAT-1 (55%)	287
Total	1202.9

EXAMPLE II

Material	Pounds
Water	306
Bentone LT	4.3
TAMOL 731—25% Active	3
VICTAWET 35B	5.7
ADVAWET 33	4
Ethylene Glycol	15
Butyl Carbitol Acetate	15
NOPCO NXZ	2
CMP Acetate	0.5
Ti Pure R-960	225
ASP 170 Clay	100
VICRON 25-11	112
CG 135	50
Water	131.5
NOPCO NXZ	2
NAT-1 (55%)	287
Total	1263

EXAMPLE III

Material	Pounds
Water	306
Bentone LT	4.3
TAMOL 731—25% Active	3
VICTAWET 35B	5.7
ADVAWET 33	4
Ethylene Glycol	15
Butyl Carbitol Acetate	15
NOPCO NXZ	2
CMP Acetate	0.5
Ti Pure R-960	225
ASP 170 Clay	100
VICRON 25-11	112
CG 135 (51%)	98
Water	83.5
NOPCO NXZ	2
NAT-1 (55%)	287
Total	1263

EXAMPLE IV

Material	Pounds
Water	315
Bentone LT	4.3
TAMOL 731—25% Active	3
VICTAWET 35B	5.7
ADVAWET 33	4
Ethylene Glycol	15
Butyl Carbitol Acetate	15
NOPCO NXZ	2
CMP Acetate	0.5
Ti Pure R-960	242.5
ASP 170 Clay	100
VICRON 25-11	112
CG 100 (46.5%)	70
Water 85	85
NOPCO NXZ	2
NAT-1 (55%)	287
Total	1263

A 13055

EXAMPLE IVA

Material	Pounds
Water	243
TAMOL 731—25% Active	3
VICTAWET 35B	6.9
ADVAWET 33	4.8
Ethylene Glycol	15
Butyl Carbitol Acetate	15
NOPCO NXZ	2
CMP Acetate	0.5
Ti Pure R-960	242.5
ASP 170 Clay	100
VICRON 25-11	93.7
CG 100 (46.5%)	107.4
Water	40
NOPCO NXZ	2
NAT-1 (55%)	285
Total	1160.8

EXAMPLE V

Material	Pounds
Water	315
Bentone LT	4.3
TAMOL 731—25% Active	3
VICTAWET 35B	5.7
ADVAWET 33	4
Ethylene Glycol	15
Butyl Carbitol Acetate	15
NOPCO NXZ	2
CMP Acetate	0.5
Ti Pure R-960	242.5
ASP 170 Clay	100
VICRON 25-11	112
CG 100 (46.5%)	70
Water	95
NOPCO NXZ	2
NAT-1 (55%)	216
PVO-44 (65%)	61
Total	1263

EXAMPLE VI

Material:	Pounds
Water	315
Bentone LT	4.3
TAMOL 731—25% Active	3
VICTAWET 35B	5.7
ADVAWET 33	4
Ethylene Glycol	15
Butyl Carbitol Acetate	15
NOPCO NXZ	2
CMP Acetate	0.5
Ti Pure R-960	242.5
ASP 170 Clay	100
VICRON 25-11	112
CG 100 (46.5%)	70
Water	90
NOPCO NXZ	2
NAT-1 (55%)	216
Polytex 611 Q (60%)	66
Total	1263

EXAMPLE VII

Material:	Pounds
Water	315
Bentone LT	4.3
TAMOL 731—25% Active	3
VICTAWET 35B	5.7
ADVAWET 33	4
Ethylene Glycol	15
Butyl Carbitol Acetate	15
NOPCO NXZ	2
CMP Acetate	0.5
Ti Pure R-960	242.5
ASP 170 Clay	100
VICRON 25-11	112
CG 100 (46.5%)	70
Water	100
NOPCO NXZ	2
UCAR-130 (58%)	272
Total	1263

EXAMPLE VIII

Material:	Pounds
Water	315
Bentone LT	4.3
TAMOL 731—25% Active	3
VICTAWET 35B	5.7
ADVAWET 33	4
Ethylene Glycol	15
Butyl Carbitol Acetate	15
NOPCO NXZ	2
CMP Acetate	0.5
Ti Pure R-960	242.5
ASP 170 Clay	100
VICRON 25-11	112
CG 100 (46.5%)	70
Water	29
NOPCO NXZ	2
Ammonium Hydroxide	2
UCAR 370 (46%)	343
Total	1265

EXAMPLE IX

Material:	Pounds
Water	225.0
Bentone LT	4.3
TAMOL 731—25% Active	3.0
VICTAWET 35B	12.7
ADVAWET 33	9.0
Ethylene Glycol	15.0
Butyl Carbitol Acetate	15.0
NOPCO NXZ	2.0
CMP Acetate	0.5
Ti Pure R-960	242.5
ASP 170	100.0
VICRON 25-11	112.2
Canadian Asbestos 6-D-20 (Canadian No. 6 shorts)	32.5
Water	326.0
NOPCO NXZ	9.0
NAT-1	285.0
Total	1393.7

The properties and characteristics of the latex paints and dried films are listed in the following table.

TABLE

	I	II	III	IV	IVA	V	VI	VIII	VIII	IX
Example:										
Viscosity (K.U.)	110	102-8	96-7	97-8	96	108	107	112	82	150
Reflectance	91	91	91	91	88	90	90	91	91	88
PVC (percent)	53.04	53.04	53.04	53.04	52.45	53.04	53.04	53.04	53.04	53.04
Contrast ratio	0.967	0.973	0.978	0.978	0.963	0.967	0.967	0.989	0.978	0.944
Solids (Percent)	54.87	52.45	52.45	52.45	56.5	52.45	52.45	52.45	52.45	48.23
Yield (gallons)	100	108	108	108	96	108	108	108	108	128.6
N.S. grind No.	7	6-5	6	5-6	5-6	5-6	5-6	5-6	5-6	0

A13656

Published by AsbestosClaims.Law
asbestosclaims.law/library/15382/25

DISCUSSION

Example 1 is a typical interior latex paint formulation (53.0% PVC, 54.9% Solids) which provides a standard measure of reflectance (91) and opacity (contrast ratio 0.967) for a 242.5 pound level of rutile titanium dioxide. The pigments in this system require 150 pounds of water to be properly dispersed leaving 226 pounds of free water. Since the asbestos has a water sorption of about 480%, the quantity that can be added is a function of the difference in water demand between the asbestos and the pigment it is replacing as well as the free water available. The lowered amount of free water lowers the amount of thickener required and this improves the flow and leveling rheology of the paint. Usually around 1–25%, preferably 7–20%, of total pigments can be replaced with the high purity type chrysotile asbestos (HPTCA).

The water demand of the asbestos and therefore the level at which it could be incorporated into latex paints could be modified by treating the product with agents, which induces hydrophobicity, such as fatty acids and their derivatives, silicones, silanes and various other materials.

A dry titanated asbestos (35% TiO_2) in pellet form was predispersed and then incorporated into the formulation of Example 2 at a 50 pound level, replacing 32.5 pounds of calcium carbonate and 17.5 pounds of the original charge of TiO_2 which is now contained on the titanated fibers. The reflectance remains at 91 and the contrast ratio was 0.973.

The asbestos has in effect predispersed the TiO_2 electrostatically along the fibers, thereby increasing its opacity when incorporated into a coating. The high brightness is quite unexpected. Asbestos has a 72% G.E. brightness and with replacement of a portion of a high brightness pigment this lower brightness material would be expected to substantially lower the reflectance of the resulting paints. The maintenance of high brightness is further indication that the asbestos fibers are electrostatically coated with the high brightness anionic pigments which hide the grayness of the fibers.

There were several indications that the fibers were not completely liberated. The grind reading decreased from 7 to 4–5 indicating the presence of some fiber bundles. The film was slightly grayer indicating some of the fibers are not completely pigmented and the surface wrinkled slightly indicating that cationic charge was available to coagulate the latex. Both of these latter effects could be due to compaction which prevents pigment deposition to satisfy the cationic surface charge of the fibers.

Example 3 is identical to Example 2, except titanated filter cake (51% solids) was substituted for the predispersed pellet and the water adjusted for the filter cake water component. The film had a reflectance of 91 and a contrast ratio of 0.978. The grind reading improved to 6 and no wrinkling was evident. Thus, the filter cake product is in a more available form, can be dispersed with conventional equipment and provides a finer grind surface.

In Example 4, the filter cake (untitanated 46.5% solids), and the titanium dioxide are added separately to the pigment dispersion. The reflectance is again 91 and the contrast ratio is 0.978. This demonstrates that the asbestos fibers are in fact coflocculating with the anionic pigments during paint manufacture.

The fibers are coflocculating with more than the titanium dioxide and the extender pigments are filling in the available spaces on the fibers. The pigment demand of the totally liberated fibers is about 900 to 1000% by weight. In Example 4A, the amount of filter cake was increased to 50 pounds. The resultant paint gave a grayish appearance when compared to the paint of Example 4. Only 342 pounds of the preferred anionic pigments are available (680%). Consequently, a portion of the asbestos fiber remained uncoated giving a discolored film.

The reflectance decreased to 88 as compared to 91 for Example 4. The contrast ratio was 0.983. Contrast ratio is defined as reflectance over a black substrate divided by the reflectance over a white substrate. The reflectance readings stated in this application are tested over a white substrate. Therefore, paints with a lower reflectance will be grayer and have a higher contrast ratio although the opacity may actually decrease as is the case in Example 4A.

The pigmented asbestos is compatible with diverse types of latex systems as well as oil and epoxy modified emulsions as shown in Examples 5 to 8. In each case, stable paints were prepared having acceptable application and working properties.

Example 9 is an attempt to prepare a similar latex paint utilizing Canadian Grade No. 6-D-20 shorts asbestos. It failed in every possible desired criteria. The Canadian asbestos could not be dispersed and gave a grind reading of 0 which is equivalent to a grind of no less than 4 mils, whereas the paints of the invention have grinds between 0.5 and 2.0 mils, equivalent to a grind number of 4 to 7, and preferably less than 2 mils.

The Canadian asbestos could not be liberated or pigmented since the film was very gray and the surface wrinkled indicating remaining available cationic charge. The high viscosity is also indicative of available cationic charge. The water content was substantially increased and the solids dropped to 48.3%, yet the viscosity was still 150 K.U. A premium quality finish paint must have a viscosity between about 70 to 125 preferably 80 to 115 K.U. The random length Canadian No. 6-D-20 asbestos fibers are incapable of complete liberation and do not cofloc with anionic pigments to form totally pigmented products in which the cationic charge of the fibers is satisfied.

The following are additional examples illustrating the invention.

	Example X	Example XI	Example XII
	9 parts TiO_2, 1 part asbestos	8.5 parts TiO_2, 1 part asbestos	10 parts TiO_2, 1 part asbestos
Ingredients:			
Water	680	680	680
Cellosize QP-4400	0.5	0.5	0.5
Tamol 731	6.0	6.0	6.0
Victawet 35-B	11.4	11.4	11.4
Advawet 33	8.0	8.0	8.0
Nopco NXZ	4.0	4.0	4.0
Ti pure R-960	576.0	576.0	576.0
Asbestos CG 100 filter cake (44% solids)	145.5	154.0	121.0
Ethylene glycol	30.0	30.0	30.0
Butyl carbitol acetate	30.0	30.0	30.0
UCAR-130	463.8	465.8	460.7
Physical properties:			
Viscosity (K.U.)	65	78	74
Reflectance	88	92.5	89
PVC (percent)	43.04	43.16	42.74
Contrast ratio	0.9785	0.9780	0.9785
Total solids (percent)	49.06	48.94	49.20
Yield (gallons)	161	162	160
N.S. grind No.	6	6	6

Referring to Examples X, XI and XII the viscosity of 65–78 for all of these compositions is within the usable range. As to reflectance, however, it is noted that Examples X and XII with ratios of pigment to asbestos of

A 15557

9 to 1 and 10 to 1 respectively have the same high reflectance values of 93, whereas Example XI, with a ratio of 8.5 pigment to 1 part asbestos, and below the 9 to 1 lower limit of the invention paint composition, has a lower reflectance of 92.5, and hence a lower brightness as compared to the paints of Examples X and XII.

Also, it is noted that Examples X and XII have a contrast ratio of 0.9785 whereas Example XI, having a pigment to asbestos ratio of 8.5 to 1, has a reduced contrast ratio of 0.9730, indicating that opacity and hiding power at a pigment to asbestos ratio of 9 to 1 or greater, are at a maximum for a given quantity of hiding pigment to asbestos, and such contrast ratio remains at such maximum with increase in the ratio of pigment to asbestos above 9 to 1, whereas such opacity and hiding power undesirably decreases at a ratio of pigment to asbestos below 9 to 1.

In summary, the particular high purity chrysotile asbestos in accordance with the invention can be completely liberated and can in this form completely cofloc with at least 9 times its weight of anionic pigment, usually 900% to 1000% by weight of anionic pigments. The pigments are dispersed along the length of the asbestos fibers and hide the relative grayness of the fibers, increasing opacity. The opacity difference is quite dramatically displayed with 1.5 mil films are observed on a hide chart.

The physical nature of the colloidal fibers with an average L/D ratio of 200 provides reinforcement by the whisker effect and improves the structural integrity of the paint film. The film has a high tensile strength and can experience large changes in substrate dimensions before the film cracks or fails. The durability, scrubbability and service life of the film are considerably enhanced.

Another desirable result is the degree of pigment dispersion attainable when the asbestos in filter cake form is incorporated into latex paints. The prior available dry Canadian fibers were limited to a maximum dispersion or grind of 3.5 mils while the filter cake yields a dispersion or grind of 1.2 mils. This is the first material which allows the use of asbestos in premium interior and exterior paints.

It is to be understood that only preferred illustrative embodiments of the invention have been disclosed and that numerous substitutions, alterations and modifications can readily be practiced by those skilled in the art without departing from the spirit and scope of the invention as defined in the following claims.

We claim:

1. An aqueous latex emulsion paint composition having a fine grind and capable of forming a film of high brightness and good opacity, consisting essentially of, by weight of said composition,

about 20 to 70% aqueous diluent;

about 5% to 50% of latex resin solids consisting essentially of a polymer of an ethylenically unsaturated monomer containing a polymerizable vinyl group;

about 4 to about 65% of pigment, said pigment including anionic pigment; and

a colloidal suspension of pigmented asbestos consisting essentially of an effective amount of short, high purity, liberated, cationic chrysotile asbestos fibrils having an ultimate fiber yield of at least 85%, a surface area of about 60 to 80 meters^2/gram, a reflectance of at least 72% and a magnetite content below 0.8%, said fibrils being pigmented with anionic pigments which are electrostatically bonded at discrete points along the length of the fibrils in a ratio of at least nine times anionic pigment to asbestos, by weight, so as to completely satisfy the cationic charge on said asbestos fibrils.

2. The paint composition according to claim 1, said paint composition containing about 5% to 25% of said latex resin solids, and having a pigment volume concentration of between about 15% and 80%, said pigment consisting essentially of about 4 to about 25% anionic pigment, and said paint composition having a grind less than 2 mils.

3. The paint composition according to claim 2 in which the polymer is selected from polymers of at least one monomer selected from the group consisting of vinyl acetate, ethyl acrylate, isobutyl acrylate, methyl methacrylate, N-butyl acrylate, methacrylic acid, N-methylol acrylamide, acrylonitrile, 2-ethylhexyl acrylate, acrylic acid, itaconic acid, styrene, butadiene, ethylene, and vinyl chloride.

4. The paint composition according to claim 2 in which the polymer is polyvinyl acetate.

5. The paint composition according to claim 2 in which the polymer is a copolymer of vinyl acetate and an acrylic ester.

6. The paint composition according to claim 2 in which said pigment includes a mixture of anionic hiding pigment and anionic extender pigment.

7. The paint composition according to claim 2 in which the polymer is polyvinyl acetate, and said pigment includes a mixture of titanium dioxide, kaolin clay and calcium carbonate.

8. The paint composition according to claim 2 in which the polymer is a copolymer of vinyl acetate and butyl acrylate, and said pigment includes a mixture of titanium dioxide, kaolin clay and calcium carbonate.

9. The paint composition according to claim 2 in which the polymer is a copolymer of ethyl acrylate, methyl methacrylate and methacrylic acid, and said pigment includes a mixture of titanium dioxide, kaolin clay and calcium carbonate.

10. The paint composition as defined in claim 3, including a thickener, a surfactant and a coalescing agent.

11. A method of forming an aqueous emulsion latex paint composition containing, by weight, about 20 to 70% aqueous diluent, about 5% to 50% by weight of anionic latex resin solids comprising a polymer of an ethylenically unsaturated monomer containing a polymerizable vinyl group, and pigment, the steps comprising:

dispersing in water, high purity, liberated, cationic chrysotile asbestos fibrils having an ultimate fiber yield of at least 85%, a surface area of about 60 to 80 meters^2/gram, a reflectance of at least 72% and a magnetite content below 0.8% to form a colloidal suspension;

adding anionic pigment to the suspension in an amount of at least nine times the weight of the asbestos to electrostatically cofloc and bond said pigments along the length of said asbestos fibrils and to completely satisfy all of the cationic charge on said fibrils;

forming a pigment dispersion containing said pigmented asbestos fibrils; and then

adding said anionic latex resin to the pigment dispersion and blending to form an intimate dispersion having a grind less than 2 mils.

12. The method according to claim 11 in which the polymer is selected from the group consisting of polymers of at least one monomer selected from the group consisting of vinyl acetate, ethyl acrylate, isobutyl acrylate, methyl methacrylate, N-butyl acrylate, methacrylic acid, N-methylol acrylamide, acrylonitrile, 2-ethylhexyl acrylate, acrylic acid, itaconic acid, styrene, butadiene, ethylene and vinyl chloride.

13. The method according to claim 11 in which the polymer is selected from the group consisting of polyvinyl acetate, a copolymer of vinyl acetate and butyl acrylate, and a copolymer of ethyl acrylate, methyl methacrylate and methacrylic acid.

14. The method according to claim 12, wherein said pigment includes a mixture of anionic hiding pigment and anionic extender pigment.

15. The method according to claim 13, wherein said pigment includes a mixture of titanium dioxide, kaolin clay and calcium carbonate.

A 13658

16. The paint composition according to claim 1, said pigmented asbestos ranging from 1% to 25% of total pigment solids.

References Cited

UNITED STATES PATENTS

3,033,808	5/1962	Murray et al.	260—29.6 R
3,214,398	10/1965	Vannoy	260—29.6 R
3,328,238	6/1967	Knowles et al.	167—16
2,833,737	5/1958	Mark et al.	260—29.6 R
2,914,495	11/1959	Gordon et al.	260—29.6 R
3,578,618	5/1971	Beardsley	260—29.6 R

HAROLD D. ANDERSON, Primary Examiner

U.S. Cl. X.R.

106—288 B; 260—17 R, 17.4 R, 23 R, 23.7 A, 27 R, 29.7 R, 29.6 RW, 29.6 H, 29.6 ME, 29.6 TA; 423—331

A13659

17- 6 7 5 :
F. J. M.
A S B

Sept. 24, 1974 J. L. MYERS ET AL 3,838,085

PIGMENTED ASBESTOS LATEX EMULSION PAINT COMPOSITION

Filed Sept. 24, 1972 2 Sheets-Sheet 1

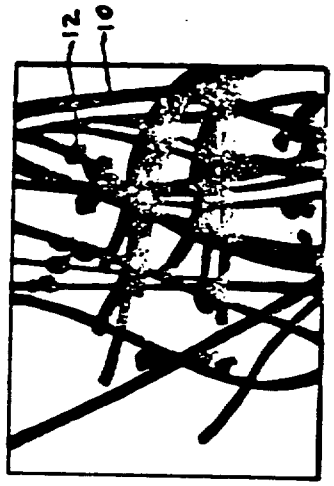


FIG. 4

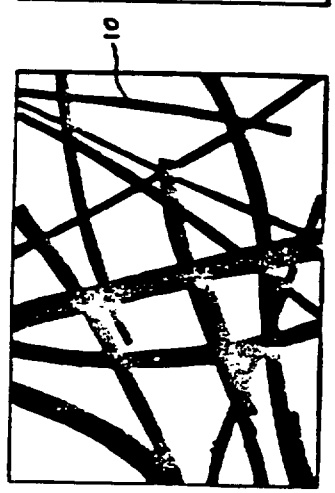


FIG. 2

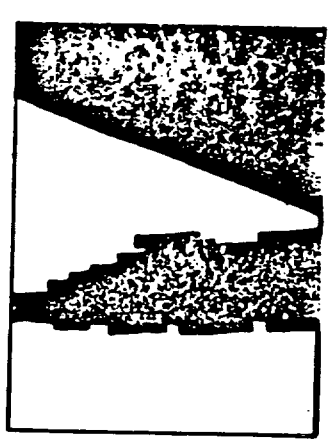


FIG. 1

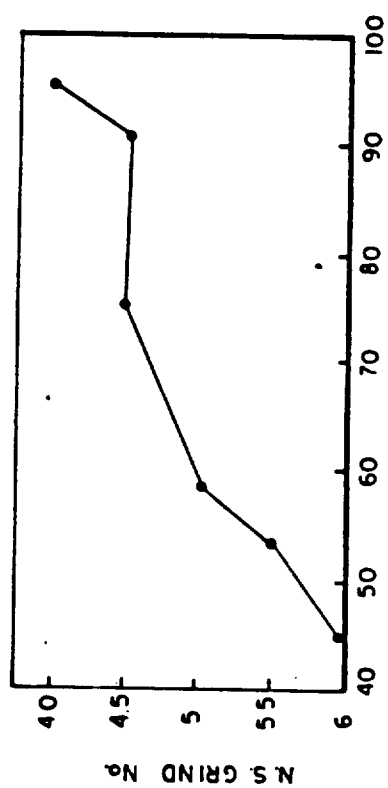


FIG. 5

INVENTORS
JOHN L MYERS
RICHARD W LASHER
RUSSELL D JAMES

BY A 13660 Finnegan, Zuelich & Thomson

ATTORNEYS

Published by AsbestosClaims.Law
asbestosclaims.law/library/15382/29

Sept. 24, 1974 J. L. MYERS ET AL 3,838,085

PIGMENTED ASBESTOS LATEX EMULSION PAINT COMPOSITION

Filed Sept. 24, 1972 2 Sheets-Sheet 2

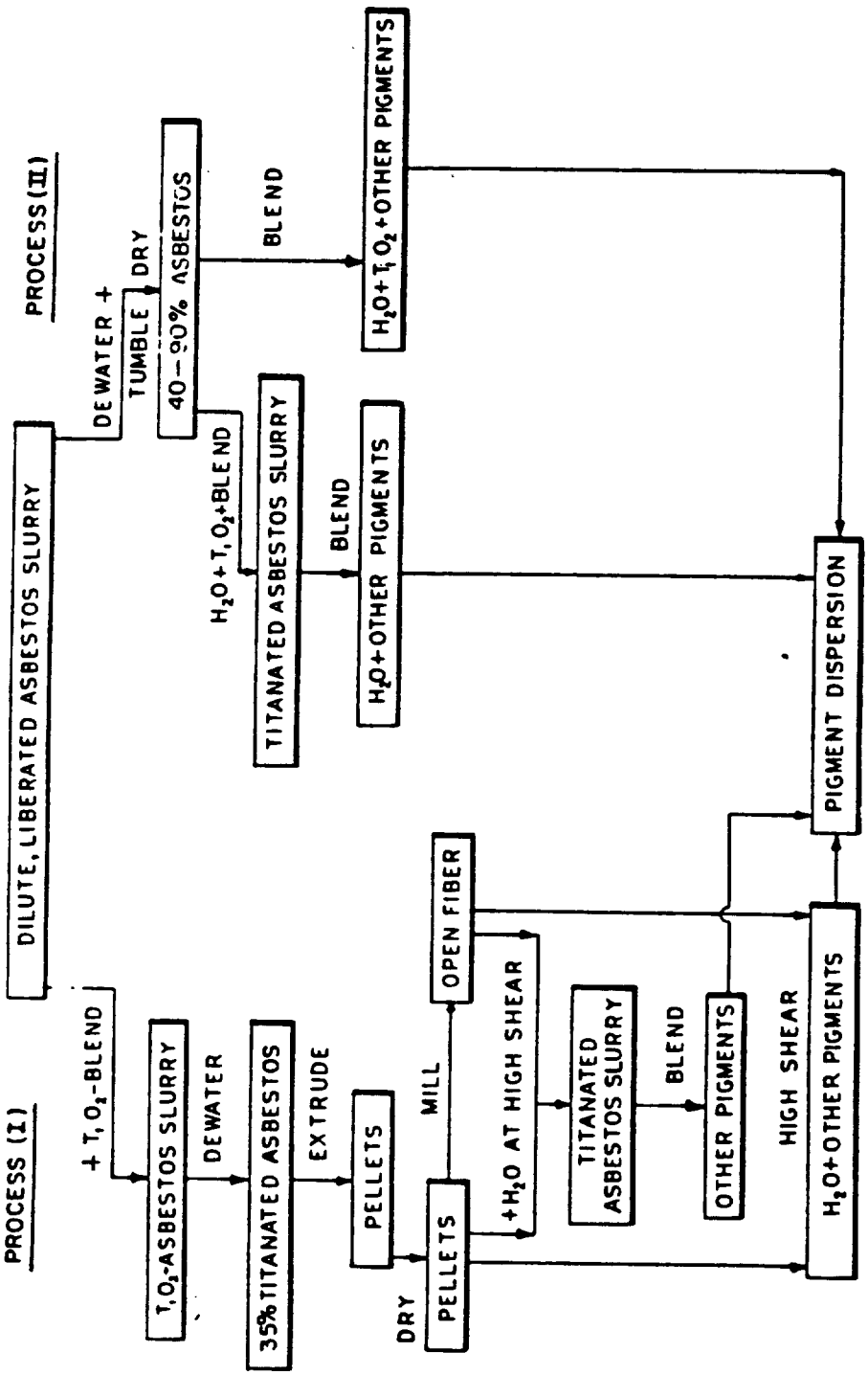


FIG. 3

INVENTORS
JOHN L. MYERS
RICHARD W. LASHER
RUSSELL D. JAMES
BY
Lindenberg, Freilich & Wasserman
ATTORNEYS.

A10861

Published by AsbestosClaims.Law
asbestosclaims.law/library/15382/30