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3,091,936

RESINOUS COMPOSITION

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This invention relates to polymerizable resinous compositions of matter capable of being rapidly cured at low temperatures to a thermoset condition. This present invention further relates to improved polyester resinous compositions comprising a mixture of an ethylenically unsaturated polyester resin and a monomeric polymerization cross-linking agent therefor, and to a process for stabilizing underground rock formations with said compositions. This invention more specifically relates to polyester resinous compositions containing a novel stabilizer-promoter system which imparts excellent stability to the uncatalyzed composition but will facilitate the rapid curing thereof at low temperatures, such as the ambient temperatures associated with underground rock formations, once the composition is contacted with a suitable free radical polymerization catalyst.

The resinous compositions of this invention are useful in a variety of applications such as in the molding, adhesive and surface coating arts, particularly where stable, rapid curing characteristics are required for the resinous component. However, as alluded to in the summary of this invention, the instant resinous compositions have been found to possess a special utility in stabilizing underground rock formations. The use of resinous materials to effect said stabilization may be found disclosed in detail in the copending application of Joseph E. Carpenter, Mine Roof Stabilization, Serial No. 698,516, dated November 25, 1957. Nevertheless, a brief discussion here of the process disclosed in said copending application will serve to aid further in an understanding of the unique properties of the compositions of this invention.

In subterranean excavation operations such as for example in the underground mining of coal, it is necessary to stabilize the rock formations which define the tunnel passage. Stabilization is particularly required of the portion that constitutes the roof or ceiling areas of the tunnel.

After a coal mining operation the roof of the subterranean passage developed generally consists of a layer of low grade coal known as roof coal. Usually overlying the roof coal layer is a layer of shale of varying thickness. The shale is in turn overlaid with a strata of sandstone which is usually well consolidated. The roof coal layer having a high content of non-combustible material is not removed in most mining operations for economic reasons. This roof coal layer is frequently not firmly bonded to the shale material above it. Shale is thin-bedded mudstone of varying degrees of compaction and strength. Like the comparatively thinner layer of roof coal, the shale layer also tends to part along its main bedding planes and as the underlying coal is removed in the mining operation, it is prone to crack athwartly and fall in chunks or slabs. Such falls are known as rock falls or roof falls and are the frequent causes of injuries and sometimes fatalities to the miners.

The individual beds of roof coal and shale can be and are customarily united together and attached in a fashion to the sandstone strata thus obviating the falling of the roof portion. A conventional way of stabilizing mine roofs consists of the use of roof bolts. In such a method, holes are drilled through the stratified layers extending partially into the sandstone formation. Metal bolts equipped with metal end plates are then suitably inserted

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therein so that the plate permanently retains the roof in position. Another method commonly observed is to timber the tunnel, in which procedure heavy timber supports are erected so as to hold up the roof portion. These prior art methods of supporting mine roofs are reasonably effective as attested by the use of these expedients for a number of years; however, there are several disadvantages residing in the use of these methods. Perhaps one of the most significant disadvantage is the high cost of the materials required for these purposes. Another disadvantage is the rather tedious and labor consuming method of installing these support means.

The aforesaid copending application describes a method of effecting stabilization of mine roofs through the use of resinous materials which serve as an adhesive for the various strata of shale and roof coal in the ceiling of the tunnel. It was found that if a small hole were drilled into the ceiling of the mine extending approximately to the solid sandstone or rock formation existing above the stratified layers and an adhesive resinous material injected into the hole with pressures varying from about 200 to 2000 pounds p.s.i., the adhesive resin would permeate the zones of weakness and upon curing effect stabilization in the area from about 5-15 feet from the hole.

The adhesive resins found to be especially suitable for this purpose are resins which are well known in the art as polyester resinous compositions. These polyester resinous compositions were found to have excellent adhesion to the subterranean formations mentioned once they were cured to a thermoset condition. While the polyester resinous compositions as known in the prior art were capable of setting up in a reasonable length of time and thus stabilization effected more effectively and quickly than with the use of bolts or timber supports, a definite need was indicated for a polyester composition which would convert extremely rapidly upon the addition of a polymerization catalyst. Additionally, this potentially quick curing resinous composition had to remain stable for longer periods of storage than customarily observed for the neat resin composition. Reconciling these diverse requirements in a single resin system obviously presents a difficult problem.

We have discovered a novel stabilizer-promoter system which when contained by the polyester resin composition will improve the stability of the uncatalyzed composition but on the other hand will nevertheless cause the resinous composition to cure extremely rapidly once contacted with a suitable catalyst. Our stabilizer-promoter system comprises a multi-component additive system of a resin inhibitor, complementary catalyst promoters and complementary polymerization stabilizers. Each and every one of the individual types of constituents contemplated for the respective components are critically required in our stabilizer-promoter system. The material we term inhibitor, which will be discussed more fully in detail hereinbelow, is a material whose presence is thought to fundamentally impart stability to the unsaturated polyester component of the resinous composition. Since these unsaturated polyester resins contain a substantial amount of polymerizable unsaturation, they are capable themselves of internally polymerizing. Any extensive amount of polymerization of the reactive resin itself will lead to the development of unsuitably high viscosities. Since effective distribution or deposition of the resin in a mine roof stabilization process, or for that matter in the many other applicable uses, is dependent on the mobile characteristics of the resin, undue viscosity buildup prior to the curing phase is undesirable. While it is believed that the inhibitor primarily functions in this manner in retarding internal polymerization of the polyester com-

ponent, it is possible that it supplements the stabilizer component in somewhat curtailing the tendency of the promoter to act as a copolymerization catalyst.

In order to achieve rapid curing of the compositions of this invention, we have found it necessary to employ a combination of distinct types of catalyst promoters with the concurrent presence of both types required to effect the curing rates contemplated herein.

As inferred above, all effective catalyst promoters exhibit in themselves some catalytic polymerization activity. Therefore, it is necessary to compensate for this behavior of the promoter prior to the time the actual polymerization catalyst is introduced into the polyester resin composition. The promoters themselves do not contain a sufficient amount of catalytic activity so that they can be regarded as primary copolymerization catalysts. Nevertheless, their catalytic potential is such which will induce gelation in the normal storage periods to which the resin composition is normally subjected. Like in the case of the promoter component, we have found that it is imperative to have a complementary system of distinct types of stabilizers for effective retardation of the catalytic effects of the promoter component. In light of this explanation of the instant stabilization-promoter system a detailed discussion of each of its components will now be entertained.

INHIBITOR

The inhibitor, that is, the material whose primary function is to retard internal polymerization of the polyester constituent of the resinous composition comprises a variety of phenolic materials which have been used heretofore for this purpose. Among such materials are phenol itself, the monoalkyl phenols, such as for example, ortho-, meta-, para-cresol, a mixture of said isomers; alkyl phenols having a plurality of such substituents as ethyl, propyl, butyl and higher alkyl radicals attached to the ring; and the like. Also the polyhydric phenols may be used such as catechol, resorcinol, hydroquinone or mixtures of these or partially alkylated polyhydric phenols, including such compounds as tertiary-butyl catechol and compounds which have several alkyl groups present. Also operable are the phenols which have alkoxy groups present such as eugenol, guaiacol and similar phenols.

The amount of inhibitor depends mainly on the amount of promoters employed and the nature of polyester resin constituent. Generally from about 0.002 to 0.02% by weight based on the mixture of reactive polyester resin and cross-linking monomer is sufficient.

THE PROMOTER

As indicated hereinabove the promoter component in accordance with this invention comprises a combination of two distinct classes or types of promoting compounds. Each of these respective types must be employed to effect rapid promotion of the catalyst in the fashion contemplated herein. In this regard it is to be mentioned that the use of any one type of promoter in excess of the amount specified, does not permit one to eliminate the need for the other type. In other words, the employment of these distinct types of promoters is in effect the utilization of two materials which are mutually promotive of one another.

One of these required promoter types comprises a cobalt salt which is capable of being dissolved in the resinous composition. Suitable soluble cobalt salts are such as cobalt naphthenate, cobalt tallate, cobalt octoate or any other higher fatty acid salt of cobalt. The amount of cobalt salt can be varied from about 0.001 to 0.3% of the salt calculated as dissolved metallic cobalt based on the total weight of the reactive resin and monomeric cross-linking agent mixture employed. On the same basis the preferred amount of cobalt metal ranges from about 0.05 to 0.15%.

The complementary promoter to be used in conjunc-

tion with the cobalt salt comprises a variety of amine promoters. Suitable amine promoters for our purposes are disclosed in U.S. Patent 2,480,928. These promoters are described therein as tertiary monoamines which contain attached to the nitrogen atom two functionally aliphatic radicals selected from the group consisting of alkyl hydrocarbons, hydroxy-substituted alkyl hydrocarbons and aralkyl hydrocarbons and one aromatic radical selected from the group consisting of aryl hydrocarbons, azo-substituted aryl hydrocarbons, amino-substituted aryl hydrocarbons, hydroxy-substituted aryl hydrocarbons, and aldehyde-substituted aryl hydrocarbons, and salts thereof. Specific examples of this class are the following: dimethylaniline, diethylaniline, di-n-propylaniline, dimethyl-p-toluidine, dimethyl-o-toluidine, dimethyl-alpha-naphthylamine, methyl benzyl aniline, p-dimethylaminoazobenzene, N,N-dimethyl-m-aminophenol, p-hydroxy-N,N-di(beta hydroxyethyl) aniline, p-dimethylaminophenyl oxalate, p-dimethylaminophenyl acetate, and p-dimethylaminobenzaldehyde. Additionally one may use in conjunction with cobalt salt a tertiary alkyl amine, a hydroxy alkyl amine or an acid salt thereof as a promoter. Exemplary of these types of promoters are diethylethylamine, triethylamine, tri-isopropylamine, trimethylamine, tri-isopropanolamine, ethyl diethanolamine hydrochloride and the like. Tertiary polyamines are also effective for use in the instant manner, such as for example, tetramethylbutanediamine. The amount of amine promoter useful in the practice of this invention varies between about 0.05 to 1.0% based on the copolymerizable mixture consisting of the reactive resin and the monomeric cross-linking material.

STABILIZER

As in the case of the promoter, the stabilizer effective in the instant invention consists of a two component system. One of these essential stabilizers is a soluble copper salt, that is, soluble in the resinous composition in the amounts contemplated for use herein. Suitable soluble copper salts include those salts of the acids mentioned hereinabove in connection with the cobalt salt. The amount of copper salt to be employed to attain the instant stability objectives ranges from 1-100 parts per million of the salt calculated as dissolved metallic copper based on the reactive resin and monomeric material. The preferred amount of copper salt on the above-indicated basis ranges from about 5-25 parts per million.

The stabilizer that is to be used in conjunction with the copper salt may be present in the amount of about 0.001 to 0.1% based on the weight of the resinous composition and preferably from about 0.01 to 0.05%. Suitable adjunct stabilizers are compounds containing a basic imino group and salts thereof. Examples of organic compounds and the salts thereof containing a basic imino group are such as the guanidines, e.g., 1,2-diphenyl guanidine; diphenyl-p-tolylguanidine hydrochloride; di-o-tolylguanidine; 1,3-dixylguanidine; 1,3-bis(2-chloro-4-methoxyphenyl) guanidine hydrobromide; ethyleneguanidine hydrochloride; 1,1'-(ethylene di-p-phenylene) diguanidine hydrochloride; 1-ethyl-1,2,3-triphenylguanidine hydrochloride; p-hydroxybenzyl guanidine; methoxyguanidine sulfate; ethylene guanidine hydrochloride; N,N-dicyclohexylguanidine hydrochloride; N,N-dicyclohexylguanidine; butyldicyclohexyl guanidine bicarbonate; octylguanidine nitrate; the isomelamines, e.g. acetamidine, bensamidine, dodecylamidine hydrochloride, acetamidine, hydrochloride; the biguanides, e.g. 1,1-bis(2-hydroxyethyl)-3,5-bis(3-methoxypropyl)-biguanide acetate, 1-(p-bromophenyl)-biguanide hydrochloride, p-chlorophenyl biguanide, (3-dibenzofuryl) methylbiguanidine, 1-p-iodophenylbiguanidine hydrochloride, (p-methoxyphenyl)-sulfanilylbiguanidine, o-tolylbiguanidine, 1-(p-chlorophenyl)-5-isopropylbiguanidine, 1-(2-dibenzofuryl)biguanidine, phenylbiguanidine hydrochloride, isopropylbiguanidine hydrochloride; the guanylureas, e.g., guanyl

(phenylsulfonyl)guanylurea, 1-guanyl-2-thioguanylurea carbonate, heptylguanylurea, 1-hexyl-1-methyl-guanylurea, (2-hydroxyethyl) guanylurea, 1-(alpha-hydroxybutyryl)guanylurea; the pseudoureas, e.g., 2-(7-chloro-4-methyl-2-guinylyl)-2-thiopseudourea hydrochloride, 2-p-cyanobenzyl-2-thiopseudourea hydrochloride, 2-cyclohexylpseudourea, 2-decylpseudourea, ethylpseudourea, 2-dodecylpseudourea hydrochloride, 2-(dodecyloxymethyl)-2-thiopseudourea hydrochloride, laurylpseudourea hydrochloride, dimethylallyl pseudourea; the pseudothiureas e.g., ethylpseudothiurea hydrochloride and ethylpseudothiurea hydrobromides, and the like.

The quaternary ammonium salts of a non-oxidizing acid at least as strong as acetic acid constitute another class of stabilizers which may be used similarly in the practice of this invention. Specific examples illustrative of this class are such as: trimethyl benzyl ammonium chloride, triethyl benzyl ammonium bromide, tributyl benzyl ammonium chloride, phenyl trimethyl ammonium chloride, ethyl pyridinium chloride, trimethyl benzyl ammonium iodide, trimethyl octyl ammonium phosphate, trimethyl benzyl ammonium oxalate, and the like. Analogous to the above mentioned ammonium salts and useful in the same manner are the quaternary phosphonium salts such as for example, tetra kis (hydroxymethyl) phosphonium chloride, trimethyl benzyl phosphonium chloride, tetra kis (1-hydroxy heptyl) phosphonium chloride, triphenylethyl phosphonium chloride, tetra kis ethyl phosphonium chloride, tetra kis methyl phosphonium bromide and the like.

As consistently mentioned hereinbefore, the resinous compositions of this invention containing the inhibitor-stabilizer-promoter system described directly hereinabove must be contacted with an addition type polymerization catalyst in order to achieve rapid curing thereof. In this connection, the rapid cure periods which are desired to be achieved range in time from about 4 to 15 minutes at 58° F. Obviously, even if one employs an effective promoter system, not all catalysts will induce the rapid cure characteristics desired at the low temperatures contemplated. Accordingly, the polymerization catalyst capable of promoting the intended rapid curing is exemplified by a large number of suitable hydroperoxide and peroxide type catalysts. A particularly preferred catalyst is methyl-ethyl-ketone peroxide. However, examples of other suitable catalysts are such as: cyclohexanone peroxide, hydroxy heptyl peroxide, 1-hydroxy cyclohexyl hydroperoxide-1, t-butyl hydroperoxide, 2,4-dichlorobenzoyl peroxide and the like. Mixtures of the peroxide and hydroperoxide type catalysts may also be used advantageously.

The polyester resin compositions which have been found to be particularly useful as adhesives in stabilizing underground rock formations as aforesaid, comprise generically those resinous compositions which result from the conjoint polymerization of a reactive unsaturated, essentially linear resin obtained by condensing an alpha, beta ethylenically unsaturated dicarboxylic acid and a polyhydric alcohol, usually a glycol, with an ethylenically unsaturated polymerizable monomer compound. These polyester compositions are well known in the art, however, further details pertaining to the specific compositions thereof and methods of preparing these compositions may be found in Ellis Patent No. 2,355,313 and Kropa Patent Nos. 2,443,735 to 2,443,741, inclusive, and additionally in the specific examples set forth hereinbelow.

In order that those skilled in the art may better understand how the present invention may be practiced, the following examples are given. These examples are set forth primarily for the purpose of illustration and any specific enumeration of details contained therein not indicated in the appended claims should not be interpreted as limitative of the instant invention. All parts specified are parts by weight unless otherwise indicated.

Example 1

Into a suitable reaction vessel equipped with stirrer, thermometer and an air-cooled reflux condenser were charged 1910 parts maleic anhydride, 1480 parts of phthalic anhydride and 2450 parts of propylene glycol. With carbon dioxide passing through the reaction mixture at a rate capable of providing an inert atmosphere above the surface of the mixture, the reactive ingredients were heated gradually with stirring to a temperature of 160° C. Heating was continued at an indicated esterification temperature until the acid number had dropped to 38. The time required to achieve this degree of condensation was approximately 20 hours. Thereupon, the reaction mixture was cooled to 80° C. and the hot polyester resin was cut with methylstyrene in the proportion of resin to methylstyrene of 70:30, respectively.

While the polycarboxylic acid component of the reactive resin of this example was a mixture of an alpha, beta ethylenically unsaturated dicarboxylic acid and a non-polymerizable dibasic acid, one may use exclusively an alpha, beta ethylenically unsaturated polycarboxylic acid such as the maleic acid of this example or any one of such acids like fumaric, aconitic, itaconic, citraconic and mesaconic or even combinations of same. Where a non-polymerizable polycarboxylic acid is employed it must be used in combination with an unsaturated acid of the type mentioned and preferably should not constitute more than 70% by weight of the total amount of the polycarboxylic acids employed. Examples of non-polymerizable acids include such as oxalic, malonic, succinic, glutaric, succinic sebacic, phthalic adipic, pimelic, submeric azelaic, tricarballic, citric, tartaric and the like. If available, the anhydrides of these acids may be substituted therefor in whole or in part.

In addition to the propylene glycol employed in the preparation of the resin of this example, one may use other types of glycols such as; ethylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol, tetraethylene glycol, butanediol-1,2, butanediol-1,3, butanediol-1,4, pentanediol-1,2, pentanediol-1,4, pentanediol-1,5, hexanediol-1,6, neopentyl glycol and the like. Polyhydric alcohols having more than two hydroxyl groups may be used, if used in combination with a predominant amount of glycol. Examples of polyols having more than two hydroxyl groups include glycerol, trimethylol ethane, trimethylol propane, pentaerythritol, dipentaerythritol, sorbitol, mannitol, adonitol, dulcitol, arabitol, xylitol, etc.

As exemplified in the formulation of the specific resin of this example, it is desirable that the polyhydric alcohol and preferably dihydric alcohol be employed in an amount which represents an excess of approximately 10-20% above the stoichiometric quantity required for a substantially complete esterification of the acid or acids employed.

The polyhydric alcohol and polyhydric acid and the various mixtures of each that may be employed should be reacted sufficiently to produce final reactive resin material having acid number desirably not greater than 60. The preferred acid number range for the resin to be employed in this invention is from about 35-40.

The cross-linking agent for the reactive resin may be any one of a number of polymerizable monomeric materials having a $\text{CH}_2=\text{C}<$ group and a boiling point in excess of about 60° C. The agent employed in this example was an isomeric mixture of ring substituted methylstyrenes. This type of substituted styrene is of particular preference in the compositions to be used as mine roof stabilizers because of its rather high flash point characteristics. The high flash point of this compound permits it to be used with relative safety in mine stabilizing application where safety requirements are of an important consideration. However, other suitable cross-linking agents include such as; styrene itself, 2,4-dimethylstyrene, 2,5-diethylstyrene and the like. Alkyl

esters of acrylic and methacrylic acids may also be used as the cross-linking material. Also, aliphatic vinyl esters may be used including vinyl acetate, vinyl butyrate, vinyl laurate, vinyl stearate, acrylonitrile, methacrylonitrile, etc. Acrylamide and methacrylamide may likewise be used. These polymerizable monomeric materials containing the $\text{CH}_2=\text{C}<$ group may be used singly or in combination with one another.

The ratio of the unsaturated polyester resin to the monomeric cross-linking agent may be varied over a wide range. The unsaturated resin content may, therefore, range from about 10 to about 90 parts to a corresponding 90 to 10 parts of polymerizable monomer. For the majority of the purposes, however, the active polymerizable components comprise from about 40 to about 60 parts by weight of the unsaturated resin and correspondingly from about 60 to 40 of the polymerizable monomeric material.

Example II

This example illustrates the type of stability characteristics associated with the uncatalyzed stabilizer-promoter systems of this invention.

To the polyester resin composition of Example 1, that is, the alkyd/methylstyrene mixture, was added 0.007% hydroquinone. To 100 gram portions of this hydroquinone inhibited composition were added the stabilizers ethylene guanidine hydrochloride and copper and the promoters consisting of cobalt and diethyl aniline in the amounts and manner as illustrated in the following table:

TABLE I

Hydroquinone	Ethylene guanidine, HCl	Copper, p.p.m. ¹	Cobalt, percent	Diethyl aniline, percent	Stability at 55° C.
0.007	None	None	None	None	less than 1 day.
0.007	0.0125	None	None	None	Do.
0.007	None	5	None	None	3-5 days.
0.007	0.0125	5	None	None	greater than 20 days.
0.007	0.0125	1	None	None	14-17 days.
0.007	0.025	1	None	None	greater than 20 days.
0.007	0.0125	5	0.1	None	11-13 days.
0.007	0.0125	20	0.1	None	11 days.
0.007	0.0125	5	0.1	0.2	5-6 days.
0.007	0.0125	20	0.1	0.2	5-6 days.

¹ As copper naphthenate.

² As cobalt naphthenate.

The stability data results indicated above were obtained for samples of the polyester resin composition subjected to an accelerated aging test. This test merely consisted of storing the respective samples in a closed container at a temperature of 55° C.

It is evident from these data that the concurrent presence of a stabilizer of an organic nature such as ethylene guanidine hydrochloride and a copper salt must be observed in order to obtain the desired storage stability characteristics. While the presence of a promoter, especially the complementary promoter system of this invention, decreases the degree stability afforded by the stabilizer component, nevertheless, when the stabilizer system is present in a manner in accordance with this invention suitable storage characteristics are to be observed.

Example III

This example primarily illustrates the beneficial effect on gelling characteristics of polyester resin compositions to be obtained in the use of the complementary promoter system of this invention.

To a sample of the polyester resin composition of Example I, was added hydroquinone in the amount of 0.007% based on the weight of the composition. To portions of this inhibited sample were added the promoter and/or stabilizer as indicated in Table II set forth hereinbelow. Each of these samples were then blended with an additional amount of methylstyrene on the basis of 20 parts of methylstyrene per 80 parts of the original blend.

To 50 gram portions of the resultant polyester resinous compositions now containing 44% total methylstyrene was added 1.5% Lupersol DDM (60% solution of methyl-ethyl ketone peroxide). Gel times for the respective samples were determined in a conventional manner consisting of submerging a glass beaker containing a sample of the resinous composition into a constant temperature water bath maintained at 58° F. The gel time indicated is the time required for a sample that is subjected to constant stirring to change from a fluid condition to a gelatinous state. As in the case of all resinous compositions of this type, the conversion from a mobile state to a gelatinous state once it begins is almost instantaneous.

TABLE II

Percent hydroquinone ¹	Percent Ethylene guanidine, HCl ¹	Copper, p.p.m. ¹	Cobalt, percent ¹	Diethyl, Aniline percent ¹	Gel time at 58° F. ²
0.007	-----	-----	-----	-----	greater than 2 hr.
0.007	0.0125	-----	-----	-----	Do.
0.007	0.0125	-----	0.1	-----	14'40"
0.007	0.0125	-----	0.1	0.2	5'30"
0.007	0.0125	5	0.1	0.2	4'55"

¹ Based on original 70/30 alkyd/methyl styrene blend.

² Original blend (80 parts) cut with an additional 20 parts of methyl styrene.

As indicated hereinbefore, it is especially desirable that a polyester resinous composition which is designed to be useful in stabilizing underground rock formations should gel at a relatively fast rate once it is contacted with the polymerization catalyst. In curing operation of the type herein concerned it is to be appreciated that the gel time of a resin is not the same as the time required to attain the insoluble and infusible characteristics to be observed for a fully cured composition. However, there is a direct relationship between the gel time evidenced by a given composition and the further time required to convert it into the thermosetting condition which is ultimately desired. In the formulation of polyester resinous compositions useful for stabilizing underground rock formations, it has been found that a gel time in the order of 6 minutes or somewhat less will ultimately cure to a thermoset condition in the time desired in said applications.

The data presented in the above Table II shows that it is necessary that the presence of a cobalt salt and an amine promoter is required to effect the required conversion. In this connection, it should be mentioned that the use of one promoter of any of the two classes contemplated will not effect a required rate of promotion. This is so even if the particular promoter is used in amounts substantially greater than that indicated as the maximum amount to be used in accordance with this invention.

In order to illustrate the bonding properties for the resinous compositions of this invention for subterranean formations analogous to those encountered in coal mining operations, the following experimental data is set forth:

Three plys of $\frac{5}{16}$ " slate were bonded together with a resinous polyester resinous composition identical with that of Example III which was employed therein determining gel time characteristics. To this resinous composition were added 0.007% hydroquinone, 0.125% ethylene guanidine hydrochloride, 5 parts per million copper (as copper naphthenate) 1000 parts per million cobalt (as cobalt naphthenate) and 0.21% diethylaniline. These additives were dissolved in the resinous composition by merely stirring the mixture. To the mixture containing the indicated stabilizer-promoter system was added 1.5% Lupersol DDM, and the catalyzed mixture was appropriately applied to the individual plys of slate. The plys were then consolidated into a test specimen and allowed to cure at 58° F. for 1½ hrs. In this curing cycle the specimen was tested for slippage of the individual slate members after 11 minutes. No slippage was observed for the test specimens of this example at the stated time. The ultimate

breaking strength of duplicate specimens were found to be 1330 and 1250 pounds respectively. The fractures in these instances were of the slate itself with the resin-slate junctures remaining intact. In order to understand the significance of the breaking strength values obtained, it is mentioned that slate of the type employed in this example without a bonding agent will break individually instead of as a unit at about 200-300 pounds.

What is claimed is:

1. A stabilized liquid thermosetting polyester resinous composition capable of rapidly curing at low temperatures to a substantially insoluble and infusible state in the presence of a free radical polymerization catalyst comprising: (1) an essentially linear polymerizable unsaturated polyester, prepared by reacting an α,β -ethylenically unsaturated dicarboxylic acid and an aliphatic diol; (2) a monomeric cross-linking agent for said (1) containing a $\text{CH}_2=\text{C}<$ group; (3) an inhibiting amount of a phenolic polymerization inhibitor; (4) a complementary promoter system of (a) from about 0.001 to 0.3% by weight of a cobalt salt, calculated as dissolved metallic cobalt, and (b) from about 0.05 to 1.0% by weight of a member selected from the group consisting of N,N-dialkylaryl tertiary amines and salts thereof; and (5) a complementary stabilizer system of (c) from about 1 to 100 parts per million by weight of a copper salt, calculated as dissolved metallic copper, and (d) from about 0.001 to 0.1% by weight of a member selected from the group consisting of guanidines, isomelamines, amidines, biguanides, guanylureas, pseudoureas, pseudothiureas, salts thereof, salts of quaternary ammonium hydroxides, and salts of quaternary phosphonium hydroxides, the amounts of said (a), (b), (c) and (d) being based on the total weight of said (1) and (2).

2. A stabilized liquid thermosetting polyester resinous composition capable of rapidly curing at low temperatures to a substantially insoluble and infusible state in the presence of a free radical polymerization catalyst comprising: (1) an essentially linear polymerizable unsaturated polyester, prepared by reacting an α,β -ethylenically unsaturated dicarboxylic acid and an aliphatic diol; (2) a monomeric cross-linking agent for said (1) containing a $\text{CH}_2=\text{C}<$ group; (3) an inhibiting amount of a phenolic polymerization inhibitor; (4) a complementary promoter system of (a) from about 0.001 to 0.3% by weight of a cobalt salt, calculated as dissolved metallic cobalt, and (b) from about 0.05 to 1.0% by weight of an N,N-dialkylaryl tertiary amine; and (5) a complementary stabilizer system of (c) from about 1 to 100 parts per million by weight of a copper salt, calculated as dissolved metallic copper, and (d) from about 0.001 to 0.1% by weight of a member selected from the group consisting of guanidines, isomelamines, amidines, biguanides, guanylureas, pseudoureas, pseudothiureas, salts thereof, salts of quaternary ammonium hydroxides, and salts of quaternary phosphonium hydroxides, the amounts of said (a), (b), (c) and (d) being based on the total weight of said (1) and (2).

3. A stabilized liquid thermosetting polyester resinous composition capable of rapidly curing at low temperatures to a substantially insoluble and infusible state in the presence of a free radical polymerization catalyst comprising: (1) an essentially linear polymerizable unsaturated polyester, prepared by reacting an α,β -ethylenically unsaturated dicarboxylic acid and an aliphatic diol; (2) a ring-substituted alkyl styrene; (3) an inhibiting amount of a phenolic polymerization inhibitor; (4) a complementary promoter system of (a) from about 0.001 to 0.3% by weight of a cobalt salt, calculated as dissolved metallic cobalt, and (b) from about 0.05 to 1.0% by weight of an N,N-dialkylaryl tertiary amine; and (5) a complementary stabilizer system of (c) from about 1 to 100 parts per million by weight of a copper salt, calculated as dissolved metallic copper, and (d) from about 0.001 to 0.1% by weight of a member se-

lected from the group consisting of guanidines, isomelamines, amidines, biguanides, guanylureas, pseudoureas, pseudothiureas, salts thereof, salts of quaternary ammonium hydroxides, and salts of quaternary phosphonium hydroxides, the amounts of said (a), (b), (c) and (d) being based on the total weight of said (1) and (2).

4. A stabilized liquid thermosetting polyester resinous composition capable of rapidly curing at low temperatures to a substantially insoluble and infusible state in the presence of a free radical polymerization catalyst comprising: (1) an essentially linear polymerizable unsaturated polyester, prepared by reacting an α,β -ethylenically unsaturated dicarboxylic acid and an aliphatic diol; (2) a ring-substituted methyl styrene; (3) an inhibiting amount of a phenolic polymerization inhibitor; (4) a complementary promoter system of (a) from about 0.001 to 0.3% by weight of a cobalt salt, calculated as dissolved metallic cobalt, and (b) from about 0.05 to 1.0% by weight of an N,N-dialkylaryl tertiary amine; and (5) a complementary stabilizer system of (c) from about 1 to 100 parts per million by weight of a copper salt, calculated as dissolved metallic copper, and (d) from about 0.001 to 0.1% by weight of a member selected from the group consisting of guanidines, isomelamines, amidines, biguanides, guanylureas, pseudoureas, pseudothiureas, salts thereof, salts of quaternary ammonium hydroxides, and salts of quaternary phosphonium hydroxides, the amounts of said (a), (b), (c) and (d) being based on the total weight of said (1) and (2).

5. A stabilized liquid thermosetting polyester resinous composition capable of rapidly curing at low temperatures to a substantially insoluble and infusible state in the presence of a free radical polymerization catalyst comprising: (1) an essentially linear polymerizable unsaturated polyester, prepared by reacting an α,β -ethylenically unsaturated dicarboxylic acid and an aliphatic diol; (2) a ring-substituted methyl styrene; (3) an inhibiting amount of a phenolic polymerization inhibitor; (4) a complementary promoter system of (a) from about 0.001 to 0.3% by weight of a cobalt salt, calculated as dissolved metallic cobalt, and (b) from about 0.05 to 1.0% by weight of an N,N-dialkylaryl tertiary amine; and (5) a complementary stabilizer system of (c) from about 1 to 100 parts per million by weight of a copper salt, calculated as dissolved metallic copper, and (d) from about 0.001 to 0.1% by weight of ethylene guanidine hydrochloride, the amounts of said (a), (b), (c) and (d) being based on the total weight of said (1) and (2).

6. A stabilized liquid thermosetting polyester resinous composition capable of rapidly curing at low temperatures to a substantially insoluble and infusible state in the presence of a free radical polymerization catalyst comprising: (1) an essentially linear polymerizable unsaturated polyester, prepared by reacting an α,β -ethylenically unsaturated dicarboxylic acid and an aliphatic diol; (2) a ring-substituted methyl styrene; (3) an inhibiting amount of a phenolic polymerization inhibitor; (4) a complementary promoter system of (a) from about 0.001 to 0.3% by weight of a cobalt salt, calculated as dissolved metallic cobalt, and (b) from about 0.05 to 1.0% by weight of an N,N-dialkylaryl tertiary amine; and (5) a complementary stabilizer system of (c) from about 1 to 100 parts per million by weight of a copper salt, calculated as dissolved metallic copper, and (d) from about 0.001 to 0.1% by weight of benzamidine hydrochloride, the amounts of said (a), (b), (c) and (d) being based on the total weight of said (1) and (2).

7. A stabilized liquid thermosetting polyester resinous composition capable of rapidly curing at low temperatures to a substantially insoluble and infusible state in the presence of a free radical polymerization catalyst comprising: (1) an essentially linear polymerizable unsaturated polyester, prepared by reacting an α,β -ethylenically unsaturated dicarboxylic acid and an aliphatic diol; (2) a ring-substituted methyl styrene; (3) an inhibiting amount

11. A stabilized liquid thermosetting polyester resinous composition capable of rapidly curing at low temperatures to a substantially insoluble and infusible state in the presence of a free radical polymerization catalyst comprising: (1) an essentially linear polymerizable unsaturated polyester, prepared by reacting an α,β -ethylenically

15. A stabilized liquid thermosetting polyester resinous composition capable of rapidly curing at low temperatures to a substantially insoluble and infusible state in the presence of a free radical polymerization catalyst comprising: (1) an essentially linear polymerizable unsaturated polyester, prepared by reacting an α,β -ethylenically un-

saturated dicarboxylic acid and an aliphatic diol; (2) styrene; (3) an inhibiting amount of hydroquinone; (4) a complementary promoter system of (a) from about 0.05 to 1.0% by weight of cobalt naphthenate, calculated as dissolved metallic cobalt, and (b) from about 0.05 to 1.0% by weight of dimethylaniline; and (5) a complementary stabilizer system of (c) from about 5 to 25 parts per million by weight of copper naphthenate, calculated as dissolved metallic copper, and (d) from about 0.01 to 0.05% by weight of benzamidine hydrochloride, the amounts of said (a), (b), (c) and (d) being based on the total weight of said (1) and (2).

16. A stabilized liquid thermosetting polyester resinous composition capable of rapidly curing at low temperatures to a substantially insoluble and infusible state in the presence of a free radical polymerization catalyst comprising: (1) an essentially linear polymerizable unsaturated polyester, prepared by reacting an α,β -ethylenically unsaturated dicarboxylic acid and an aliphatic diol; (2) styrene; (3) an inhibiting amount of hydroquinone; (4) a complementary promoter system of (a) from about 0.05 to 1.0% by weight of cobalt naphthenate, calculated as dissolved metallic cobalt, and (b) from about 0.05 to 1.0% by weight of dimethylaniline; and (5) a complementary stabilizer system of (c) from about 5 to 25 parts per million by weight of copper naphthenate, calculated as dissolved metallic copper, and (d) from about 0.01 to 0.05% by weight of trimethylbenzyl ammonium chloride, the amounts of said (a), (b), (c) and (d) being based on the total weight of said (1) and (2).

17. A method of stabilizing an underground rock formation having zones of weakness which comprises drilling a hole into said formation and injecting into said hole a liquid thermosetting polyester resinous composition comprising: (1) an essentially linear polymerizable unsaturated polyester, prepared by reacting an α,β -ethylenically unsaturated dicarboxylic acid and an aliphatic diol (2) a monomeric cross-linking agent for said (1) containing a $\text{CH}_2=\text{C}<$ group; (3) an inhibiting amount of a phenolic polymerization inhibitor; (4) a complementary promoter system of (a) from about 0.001 to 0.3% by weight of a cobalt salt, calculated as dissolved metallic cobalt, and (b) from about 0.05 to 1.0% by weight of a member selected from the group consisting of N,N-dialkylaryl tertiary amines and salts thereof; (5) a complementary stabilizer system of (c) from about 1 to 100 parts per million by weight of a copper salt, calculated as dissolved metallic copper, and (d) from about 0.001 to 0.1% by weight of a member selected from the group consisting of guanidines, isomelamines, amidines, biguanides, guanylureas, pseudoureas, pseudothioureas, salts thereof, salts of quaternary ammonium hydroxides and salts of quaternary phosphonium hydroxides; and (6) a free radical polymerization catalyst, the amounts of said (a), (b), (c) and (d) being based on the total weight of said (1) and (2), whereby said resinous composition flows into said zones of weakness and cures in position, thereby adhesively uniting said formation at said zones of weakness.

18. A method of stabilizing an underground rock formation having zones of weakness which comprises drilling a hole into said formation and injecting into said hole a liquid thermosetting polyester resinous composition comprising: (1) an essentially linear polymerizable unsaturated polyester, prepared by reacting an α,β -ethylenically unsaturated dicarboxylic acid and an aliphatic diol; (2) a ring-substituted methyl styrene; (3) an inhibiting amount of a phenolic polymerization inhibitor; (4) a complementary promoter system of (a) from about 0.001 to 0.3% by weight of a cobalt salt, calculated as dissolved metallic cobalt, and (b) from about 0.05 to 1.0% by weight of an N,N-dialkylaryl tertiary amine; (5) a complementary stabilizer system of (c) from about 1 to 100 parts per million by weight of a copper salt, calculated as dissolved metallic copper, and (d) from about 0.001 to

0.1% by weight of a member selected from the group consisting of guanidines, isomelamines, amidines, biguanides, guanylureas, pseudoureas, pseudothioureas, salts thereof, salts of quaternary ammonium hydroxides and salts of quaternary phosphonium hydroxides; and (6) a free radical polymerization catalyst, the amounts of said (a), (b), (c) and (d) being based on the total weight of said (1) and (2), whereby said resinous composition flows into said zones of weakness and cures in position, thereby adhesively uniting said formation at said zones of weakness.

19. A method of stabilizing an underground rock formation having zones of weakness which comprises drilling a hole into said formation and injecting into said hole a liquid thermosetting polyester resinous composition comprising: (1) an essentially linear polymerizable unsaturated polyester, prepared by reacting an α,β -ethylenically unsaturated dicarboxylic acid and an aliphatic diol; (2) styrene; (3) an inhibiting amount of a phenolic polymerization inhibitor; (4) a complementary promoter system of (a) from about 0.001 to 0.3% by weight of a cobalt salt, calculated as dissolved metallic cobalt, and (b) from about 0.05 to 1.0% by weight of an N,N-dialkylaryl tertiary amine; (5) a complementary stabilizer system of (c) from about 1 to 100 parts per million by weight of a copper salt, calculated as dissolved metallic copper, and (d) from about 0.001 to 0.1% by weight of a member selected from the group consisting of guanidines, isomelamines, amidines, biguanides, guanylureas, pseudoureas, pseudothioureas, salts thereof, salts of quaternary ammonium hydroxides and salts of quaternary phosphonium hydroxides; and (6) a free radical polymerization catalyst, the amounts of said (a), (b), (c) and (d) being based on the total weight of said (1) and (2), whereby said resinous composition flows into said zones of weakness and cures in position, thereby adhesively uniting said formation at said zones of weakness.

20. A method of stabilizing an underground rock formation having zones of weakness which comprises drilling a hole into said formation and injecting into said hole a liquid thermosetting polyester resinous composition comprising: (1) an essentially linear polymerizable unsaturated polyester, prepared by reacting an α,β -ethylenically unsaturated dicarboxylic acid and an aliphatic diol; (2) a ring-substituted methyl styrene; (3) an inhibiting amount of hydroquinone; (4) a complementary promoter system of (a) from about 0.05 to 1.0% by weight of cobalt naphthenate, calculated as dissolved metallic cobalt, and (b) from about 0.05 to 1.0% by weight of dimethylaniline; (5) a complementary stabilizer system of (c) from about 5 to 25 parts per million by weight of copper naphthenate, calculated as dissolved metallic copper, and (d) from about 0.01 to 0.05% by weight of ethylene guanidine hydrochloride; and (6) a peroxide polymerization catalyst, the amounts of said (a), (b), (c) and (d) being based on the total weight of said (1) and (2), whereby said resinous composition flows into said zones of weakness and cures in position, thereby adhesively uniting said formation at said zones of weakness.

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