June 28, 1966 F. WHITTIER ETAL 3,258,032

COATING

Filed July 14, 1961

Fig. 1.

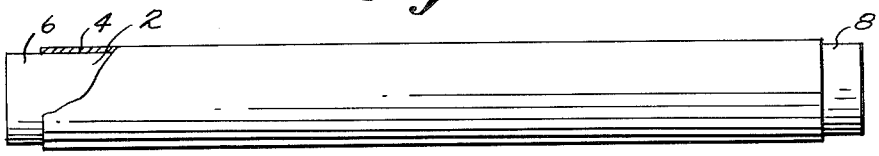


Fig. 2.

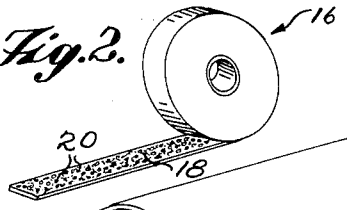


Fig. 3.

Fig. 4.

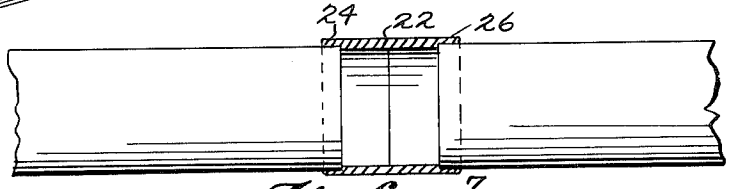


Fig. 5.

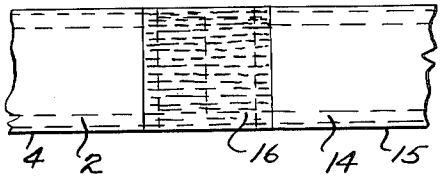


Fig. 6.

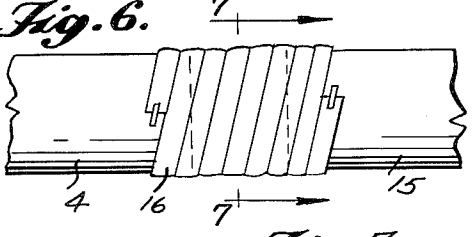


Fig. 8.

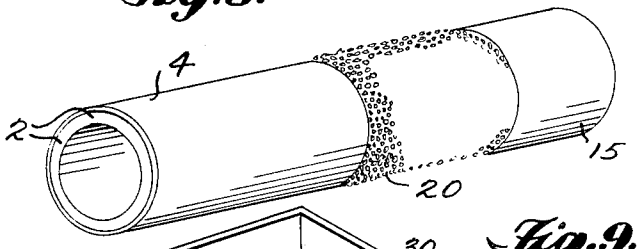


Fig. 7.

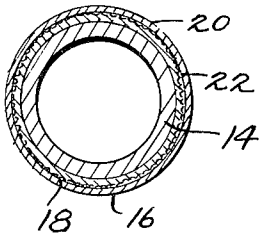
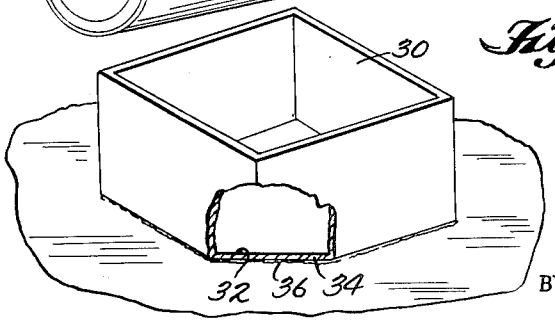


Fig. 9.



INVENTORS

FREDERICK WHITTIER

NORMAN T. SHIDELER

BY Cushman Darby & Cushman

ATTORNEYS

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3,258,032

COATING

Frederick Whittier, Pittsburgh, Pa., and Norman T. Shideler, deceased, late of Pittsburgh, Pa., by Susan J. Shideler, executrix, Pittsburgh, Pa., assignors, by mesne assignments, to United States Steel Corporation, a corporation of Delaware

Filed July 14, 1961, Ser. No. 124,233
6 Claims. (Cl. 138—146)

This invention relates to the application of a granular filler to a coating on a pipe or flat surface.

It is an object of the present invention to develop a means for treating coated pipe where the coating requires drying time, set time or curing time whereby the coated pipe can be immediately handled, walked on and/or lowered into the pipe trench and backfilled without damage to the wet coating.

Another object is to insure against displacement of, movement of, or other damage to set of, the wet coating.

A further object is to prepare improved coating pipes wherein the coating has greater strength, less tendency to move under pressure, better heat stability and greater puncture resistance.

An additional object is to devise an improved procedure for applying granules to flat and other surfaces.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

A preferred procedure for accomplishing the objects of the present invention is to provide a film or other tape to one side of which is applied a film of adhesive. Onto this adhesive is applied a granular filler of appropriate particle size, e.g., 5 to 100 mil diameter, preferably of a single particle layer. The appropriate section of a pipe having a coating comprising a thermosetting material, or even a material which is hardenable on cooling is also provided. The granular particle coated tape is then applied over the coating. The pipe can then be installed without damage to the unset coating. The coating can then be cured or otherwise allowed to set. It has been found desirable that the adherence of the adhesive on the tape for the filler particles be less than the adherence of the set coating on the pipe for the filler in order that the filler particles become locked in the pipe coating.

The invention will be best understood in connection with the accompanying drawings wherein:

FIGURE 1 is a side elevation partially in section of a coated pipe;

FIGURE 2 is a perspective view of a particle coated tape;

FIGURE 3 is a perspective view of a pair of welded pipes prior to applying the particle coated tape;

FIGURE 4 is a side elevation of a pair of pipes having an over-all set coating and a settable coating in the joint area;

FIGURE 5 is a view similar to FIGURE 4 having a tape covering the settable coating;

FIGURE 6 is a side elevation showing a preferred method of applying the tape;

FIGURE 7 is a sectional view taken along the line 7—7 of FIGURE 6;

FIGURE 8 is a perspective view of the joined pipes of FIGURE 6 but having the tape removed; and

FIGURE 9 is a plan view of an alternative form of the invention.

Referring more specifically to the drawings, there is provided a cylindrical pipe 2 (FIGURE 1) having a 20 mil thick cured or hardened coating 4 made from 30 parts of an epoxy ether resin from bisphenol A and epichlorhydrin (melting point 9° C. and epoxy value 0.50), 30 parts coal tar pitch, 9 parts mica, 10 parts talc, 1 part hydrated silica (Cabosil). The curing agent for the resin was 6.5 parts of tri(dimethylaminomethyl)phenol. Three inches at the ends 6 and 8 of pipe 2 are left uncoated. The uncoated end 8 of pipe 2 is welded at 10 to the uncoated end 12 of cylindrical pipe 14. It will be observed that the main portion of pipe 14 has a coating 15 of the same cured epoxy resin-coal tar pitch composition as pipe 2.

There is further provided a roll of two inch masking tape 16, e.g., of crinkly kraft paper having an adhesive, e.g., a pressure sensitive adhesive made from a vulcanized pasty rubber as set forth in Example 3 of Kellgren patent 2,410,079, on inner side 18 thereof. (The term pressure sensitive adhesive as used in the instant specification and claims is used in its normal sense as set forth in Kellgren, column 1, lines 1–14.) The tape is unrolled and 24 to 28 mil diameter sandblast sand 20 is sifted onto the adhesive side 18 of the tape. The tape is then rerolled so that the excess sand is discharged leaving a single layer of sand on the roll of tape.

After welding, the uncoated areas 8 and 12 at the joint of pipes 2 and 14 are cleaned and given a heavy coat 22, e.g., 20 mils, of the same coal tar-epoxy resin with amine curing agent as applied to the main portions of the pipes. The coating 22 is applied not only to the bare pipe joint but extends over the pipe coatings 4 and 15, respectively, at 24 and 26 for about one inch. The prepared tape 16 is spirally wound with the sand coated side down, as shown in FIGURE 6, on the still wet coating 22, keeping tension on the tape and wrapping with approximately a ¼ inch overlap. When the last of the wet coating 22 is covered, the tape 16 is cut off and the loose end taped in place with an adhesive. The pipe thus welded and with the coated unset joint may be handled, walked on, rolled or installed by lowering into the pipe trench and backfilling without damage to the unset coating 22. In addition, the final cured coating film 22 is greatly strengthened, has less tendency to move under pressure and has greater puncture resistance.

The hard sand particles are surrounded by the coating and since they are in intimate contact with each other and the pipe surface prevent damage to the coating. Final curing of the coating film 22 can be accomplished either before or after installation of the pipe. After setting of the coating, the tape 16 can be removed, but the sand particles remain locked in cured coating 22.

The backing for the tape 16 can be crinkly kraft as described in connection with the drawing or can be polyethylene, polypropylene, vinyl chloride polymer, vinyl acetate-vinyl chloride copolymer or other vinyl resin, polyethylene terephthalate, cloth, glass cloth, etc. Preferably, the tape is made of a slightly elastic material to permit tight wrapping without buckling because of the lap.

The thickness of the film backing of the adhesive tape is not critical. The specific adhesive also is not critical, although, as previously stated, the adherence of the adhesive on the tape for the filler particles should be less than the adherence of the pipe coating when set for the filler. Typical of the suitable adhesives are those set forth in the aforementioned Kellgren patent, as well as those described in Drew Patent 2,177,627.

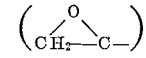
As previously indicated, onto the adhesive on the tape is sifted or spread in other manner suitable sized particles that adhere in a single particle layer to the adhesive. Ap-

propriate sized particles include silica sand, garnet, emery, Carborundum, aluminum oxide, slate, roofing granules, etc. Preferably, the particles have a hardness of at least 3 on the Mohs scale. The size of the particles determines the thickness of the coating.

The adhesive can be applied to the tape backing followed by sifting an excess of the sized granules onto the adhesive as the film or tape is unrolled. Concurrently, the formed final tape can be slit to proper width and rerolled into rolls such that excess granules drop off. These are collected and reused.

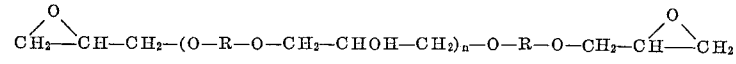
The pipe can be coated with any appropriate resin composition which can be set. The preferred resin compositions are the coal tar pitch-epoxy resins set forth in Whittier et al. Patent 2,765,288.

The epoxy ethers or resins, suitable for use in the compositions of the invention, correspond with those described in U.S. Patent Nos. 2,528,417, of October 31, 1950, and 2,500,449, of March 14, 1950, i.e., they contain along with ethereal oxygen, glycidyl groups in such quantity that the material has a 1,2-epoxy equivalency in the average molecule, of greater than one. By the epoxy equivalency, reference is made to the average number of 1,2-epoxy groups



contained in the average molecule of the ether.

A preferred group of epoxy ethers for use in the invention is prepared by reacting a dihydric phenol with epichlorhydrin in alkaline solution. These products are of resinous character and are either solid or liquid materials at normal temperature (20–30° C.). Any of the various dihydric phenols are used in preparing these glycidyl ethers, including mononuclear phenols like resorcinol, catechol, hydroquinone, etc., or polynuclear phenols like bis-(4-hydroxyphenyl)-2,2-propane (bis-phenol), 4,4'-dihydroxy benzophenone, bis-(4-hydroxyphenyl)-1,1-ethane, bis-(4-hydroxyphenyl)-1,1-isobutane, bis-(4-hydroxyphenyl)-2,2-butane, bis-(4-hydroxy-2-methylphenyl)-2,2-propane, bis-(hydroxy-2-tertiary butyl phenyl)-2,2-propane, bis-(2-dihydroxy-naphthyl)-methane, 1,5-dihydroxy naphthalene, etc. The product may be represented by the formula:



wherein n is an integer, preferably from 0 to 7, and R represents the divalent hydrocarbon radical of the dihydric phenol. The preferred epoxy ethers for use in the invention are those having epoxy values no less than 0.20 (Pyridinium chloride method), and melting points no greater than 80° C. (Durran's mercury method). The preferred phenol is bis-phenol A.

Other polyhydric phenols can be employed including novolaks prepared from phenol and formaldehyde or from cresol and formaldehyde.

There can be used 1,2-epoxy-containing polyethers of polyhydric alcohols, such as polyglycidyl ethers thereof, like the diglycidyl ether of ethylene glycol, propylene glycol, trimethylene glycol, diethylene glycol, triethylene glycol, glycerol, dipropylene glycol and the like. Other typical ethers of this class include glycidyl ethers of polyhydric alcohols having a 1,2-epoxy equivalency greater than one, such as the polyglycidyl ethers of glycol, diglycerol, erythritol, pentaglycerol, mannitol, sorbitol polyallyl alcohol, polyvinyl alcohol, and the like.

In general, the glycidyl ether resin will contain at least one epoxy group and usually less than two per molecule. The epoxy equivalency may be defined as the number of grams of resin containing one gram equivalent of epoxide.

Any of the conventional curing agents can be employed. For this purpose, there may be used small amounts of poly-functional amines, such as ethylene di-

amine, ethylene triamine, benzyl dimethylamine, 3-dimethylaminopropylamine, 3 - diethylaminopropylamine, tetraethylene pentamine and the like.

Additional curing agents include N-hydroxyethyl diethylenetriamine, tri(dimethylaminomethyl)phenol, m-phenylenediamine, dicyandiamide, melamine, triethylene tetramine, piperazine, diacetone diamine, 4,4'-diaminodiphenyl sulfone, soduim hydroxide, potassium hydroxide, sodium phenoxide, acid materials preferably having a plurality of acid groups, e.g., oxalic acid, phthalic anhydride, citric acid, tricarbyllic acid, aconitic acid, itaconic acid, malic acid, diglycollic acid, phosphoric acid, n-butyl dihydrogen phosphate, diethyl ortho phosphate, hexaethyl tetraphosphate, Friedel-Crafts metal halides, e.g., aluminum chloride, zinc chloride, ferric chloride, boron trifluoride, boron-fluoridediethyl ether complex, boron-fluoride-phenol complex, diisocyanates, e.g., 2,4-toluene diisocyanate, and polyamides, e.g., long chain fatty acid amides such as Versamid 115 and Versamid 125.

Amines and amides having at least 5 carbon atoms are often especially effective.

The curing agents may be used in various amounts, although they are usually employed in the range of from 0.05 to 0.25 part per part by weight of epoxy ether resin. The preferred epoxy resins may be set into a cured state simply by the addition thereto of the curing agent at ambient temperatures, e.g., 10 to 60° C., and, hence, these two ingredients are usually kept separated until just before application of the composition to the surface to be coated, e.g., the metal or concrete surface or pipe line joints.

Generally, from 10 to 90 parts of epoxy resin and 90 to 10 parts of the coal tar pitch are employed based on 100 parts by weight of the total epoxy resin-pitch content, with 15 to 50 parts of resin and 85 to 50 parts of pitch being preferred.

The coal tar pitch can be blended alone with the epoxy resin or the coal tar pitch can be employed in a solvent, e.g., aromatic hydrocarbons such as high flash naphtha, xylene, toluene, creosote oil, etc. Coal tar itself can be employed as the source of coal tar pitch since coal tar, both before and after taking off the lower boiling fractions contains coal tar pitch.

In place of the epoxy resin coating for the pipe there can be employed thermosetting coatings such as phenol-formaldehyde, urea-formaldehyde, melamine-formaldehyde, cross-linked polyesters such as styrene modified maleic anhydride-propylene glycol and diallyl phthalate modified fumaric acid-ethylene glycol. There can also be employed thermoplastic materials, e.g., polyvinyl chloride, vinyl chloride-vinyl acetate copolymer, polyethylene, polypropylene, polyethylene terephthalate, nylon, e.g., polymeric hexamethylene adipamide. In such case the adhesive tape coated with the filler granules should be applied while the resin is still in the liquid or pasty condition before the resin has cooled enough to set.

The system of the present invention can also be employed to apply a coating of granules of uniform thickness to flat or other surfaces and/or to produce a protective coating and nonskid surface. In this case, the surface may receive an initial barrier coating of the desired coating, e.g., coal tar pitch-epoxy resin, that is allowed to set. Alternatively, the initial barrier coat is omitted and the wet coal tar pitch-epoxy resin coating, for example, is directly applied to the desired surface and before setting is treated with the granule containing adhesive tape. The tape can be employed in the form of elastic or nonelastic sheets or rolls of any desired width and comprising an appropriate backing, adhesive and selected sized granules as described above.

Specifically, as shown in FIGURE 9, a rectangular cardboard **30** was coated on the bottom surface **32** with a thin coating **34** of a coal tar pitch-epoxy resin and while the resin was still in the wet curable state a sand coated adhesive tape, as shown in FIGURE 2, was applied to the bottom surface **32**. A light rubber roller was worked over the surface of the tape to thoroughly embed the sand into the wet coating. When the coating had cured, the tape backing was stripped from the surface **32** leaving a monomolecular granular layer **36** firmly embedded in the coating to produce a uniform coating thickness and a nonskid surface.

It is not necessary to lap edges of sheets in the above process but they can be butt jointed together.

The composition of the present invention can be employed in coating roadways, airplane runways, stair treads and other pedestrian and vehicular pavements.

When utilizing copper-copper oxide, cobalt or the like, for example, as the granular filler the composition can be employed to coat ship hulls and other structures to impart anti-fouling properties.

We claim:

1. An article having a surface, a protective coating comprising a settable resin on said surface, a single particle thick layer of a granular filler at least partially embedded in said coating, and a tape external of said surface and said filler also being adhered to said tape.

2. An article according to claim **1** wherein said settable resin is in set condition and the adherence of said granular filler to said set resin is greater than the adherence of said granular filler to said tape, whereby said tape can be removed without removing said granular filler.

3. A pipe having a settable resin protective coating on a surface thereof, a single particle thick layer of a granular filler at least partially embedded in said coating, and a tape separated from said surface by said filler, said filler also being adhered to said tape.

4. A cylindrical pipe having a settable resin protective coating on the external surface thereof, a single particle thick layer of a granular filler at least partially embedded in said coating and a tape external of said surface separated from said surface by said filler, said filler also being adhered to said tape.

5. A pipe according to claim **4** wherein said settable resin is in set condition and the adherence of said granular filler to said set resin is greater than the adherence of said granular filler to said tape.

6. A pipe according to claim **5** wherein said resin comprises a coal tar pitch-epoxy resin combination.

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EARL M. BERGERT, *Primary Examiner.*

DOUGLAS J. DRUMMOND, *Examiner.*