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PRIMER FOR PLASTICIZED COAL TAR ENAMELS AND METHOD OF PRODUCING SAME

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The present invention relates to a coal tar base primer for plasticized coal tar enamels and a process for producing the same. The primary object of the invention is to produce an improved primer of the character in question, having quick drying time, great resistance to shelf life degradation and improved, more reliable and uniform characteristics as contrasted with such primers known prior to our invention.

For many years it has been known that plasticized coal tar enamels are highly effective for the protection of the surfaces of metal—and particularly ferrous metal—articles including pipes and conduit; but it has long been recognized that satisfactory adherence of such enamels to such surfaces necessarily requires the interposition of some sort of primer coat. Although industry has diligently sought a satisfactory primer for such use and various coal tar base primers have been commercially used for that purpose, even the best of those primers heretofore known have been variable in quality and thus have not been uniformly reliable, either in the manufacturing process or in use.

Plasticized coal tar enamel is commercially produced by intimately mixing coal tar pitch, high boiling point aromatic oils and finely-divided bituminous coal and then digesting the mixture at 300°–315° C. with agitation. During such digestion, the mixture undergoes a change suggestive of solution of the coal in the hot melted pitch. The pitch is said to be plasticized by the coal in the process, and it is evident that there is some affinity between the components since the coal will not flocculate or otherwise precipitate from the mixture on standing in melted condition. This plasticized pitch, after the addition of a suitable filler such as, for instance, powdered talc, is known as coal tar enamel.

While many different kinds of coal tar base primers have been used, over the years, in connection with such enamels, with varying degrees of success, perhaps the most nearly-satisfactory of such previously-known primers for plasticized enamels are the ones disclosed in Patent No. 2,228,102, issued January 7, 1941, upon the application of Frank W. Yeager, and in Patent No. 2,752.267, issued June 26, 1956, on the application of Norman T. Shideler. Even these primers, however, are found to be quite unpredictable in use, performing quite effectively at times but failing at other times, and frequently without any readily perceptible reason for failure.

We have discovered that the previously unpredictable behavior of primers heretofore commercially available is actually predictable upon the basis of the time-temperature exposure of the product beginning when the coal tar primer base is dispersed in the solvent naphtha vehicle.

We have observed that in fact a primer formulation according to Yeager and others has an ability to withstand time and temperature before expiring that is fairly constant from one batch to another if the time and temperature exposure is measured from the moment that the melted pitch and solvent are brought together. The total time for such a product to become useless may be drastically shortened by exposure of the batch to heat as taught by Yeager, especially in the initial dispersion phase or at any time subsequent to that phase and before the primer is applied and permitted to dry. Ultimate variations in quality of performance appear to be induced by variables such as temperature of the hot pitch, heat capacity of the batch as a function of its total weight and average temperature, heat capacity of equipment as a function of its temperature, and heat generated by mechanically stirring the batch. Degradation of the primers here under consideration by exposure to heat is irreversible; that is, if heat is permitted to reach the coal tar primer base while in contact with a polar, volatile vehicle such as, for instance, coal tar solvent naphtha, nothing can be done to reconstitute or repair the damage. The effects of heat exposure are cumulative. The total time, from the moment that the coal tar primer base is mixed with the vehicle until the resulting primer becomes unsuitable for the purpose intended, seems to follow a relationship that involves the logarithm of time and, inversely, the temperature. Roughly, it may be said that in the case of temperatures above 100° F. such a primer degrades at a rate that is a function of temperature and the logarithm of time according to the formula:

$$L=\text{antilog}\ [-(t_1-t_0)\times.02+2]$$

where:

L=Shelf life in days
t_1=Average effective shelf temperature ° F.
t_0=100° F.

or, expressed differently:

$$L=10{,}000e^{-.0461t_1}$$

e=Base of natural logarithm=2.71828

After this behavior of coal tar primer base in the presence of coal tar solvent naphtha vehicle was observed, the explanation of the variable character of primers produced under the prior art became clear, and as a result we have discovered how to prepare these primers without encountering the degrading effects of heat, and thus have discovered a new process and a new product in that the product that we hereinafter describe has not been degraded by exposure to heat. Others have observed that any coal tar primer for plasticized enamel will expire on standing at elevated temperatures or finally at atmospheric temperatures, but we have discovered that by storage at reduced temperatures, the time of expiration may be postponed almost indefinitely.

It is our present theory that, when the coal tar pitch base is in contact with such a vehicle at temperatures significantly above 100° F. two phenomena occur that contribute to the degradation of the primer. One is an attack by the coal tar solvent naphtha onto the finite particles of the primer base causing "agglutination" at the surface of the primer base particles.

We have observed the effect under the microscope, and it is evident by the appearance of an amber envelope or shell around the finite particles in primers. In the case of primers made according to our discovery, this amber envelope is very faintly perceptible, and very thin as compared to the size of primer base particles, which are black. In primers that have been degraded, the amber envelope is much greater in thickness and the coal tar primer base particles are much smaller by comparison. It is our belief that coal tar solvent naphtha absorbs into the primer base particle by the effect of heat and cannot escape readily when the primer is applied to surfaces and thereby contributes to much slower drying time of the primer.

The other effect mentioned above is one actually of solubility of some fractions of coal tar primer base particles into the vehicle as a consequence of exposure of the mass to raised temperature. Once the vehicle has been contaminated by fractions of the coal tar pitch base, on evaporation, a film of coal tar chemicals soluble in coal tar solvent naphtha is laid down in such a way that

bond development with the hot enamel is impaired, and the bond that does develop, such as it is, is not stable, becoming increasingly weaker on exposure in service.

Whatever may be the reason, we have found that if a primer of the character here under consideration is produced by fragmentizing solidified plasticized coal tar pitch primer base, adding thereto a suitable fluent, polar, volatile vehicle such as, for instance, coal tar naphtha and subjecting the mixture to contritional action while maintaining the temperature of the mass always below 100° F., there results a thixotropic mixture which possesses all of the desirable characteristics of a primer for a plasticized coal tar enamel, which will have quick drying properties, perform uniformly and which possesses a shelf life which exceeds that of any such primer heretofore known.

Extended experimentation has established the fact that a primer so produced will unfailingly give strong adhesion between the properly applied plasticized coal tar enamel film and the surface to be protected. Articles coated with plasticized coal tar enamel over primer prepared in accordance with the present invention have repeatedly been exposed at 160° F. for periods of seventy-two hours without any perceptible loss of the bond strength of the coat. Primer prepared in accordance with the present invention has been stored in closed containers at an effective average atmospheric temperature of 70° F. for periods of one year or more, and has then been used, in accordance with commercial practice, as a bond for a plasticized coal tar enamel, with uniformly satisfactory results.

It is an essential requirement that the coal tar pitch and the fluent vehicle shall be cool when they are first brought into mutual contact and that the temperature thereof shall not be permitted to rise above, for instance, 120° F. even momentarily during the mixing and contritional operation. Brief periods of temperatures in the range between 100 and 120° F. are not intolerable, but exposure of the mixture to temperatures as high as 120° F. should not be continued for longer than approximately thirty minutes.

We have found that the temperature may vary rather widely and erratically within the body of the mass during the mixing operation. This appears to be the result of the mechanical equivalent of heat as energy is expended to reduce the base pitch to its ultimate particle size and the comparatively low coefficient of heat conductivity of solid pitch. The freshly exposed surfaces that result from reducing the particle size in a mill appear to be very reactive to polar vehicles if the temperature is permitted to rise. Thus, not only must the mean temperature of the mass be held below the above-stated limits, but also care must be taken to prevent any even minute points within the mass from reaching a temperature equivalent to the softening temperature of the pitch even momentarily, and to prevent even any such minute portion from maintaining a temperature above approximately 120° F. for any appreciable period of time.

The mixing and contritional action upon the fragmentized pitch and the vehicle may advantageously be carried on in a conventional ball mill; but we have found that, in order to inhibit the production of "hot spots" within the mass of material, it is desirable to use ceramic balls rather than metallic balls in such a mill. Furthermore, we presently believe that, even under such conditions, it will usually be necessary to provide external cooling means for the mill in order that heat may be extracted from the mass, during the contritional operation, to insure against undue elevation of temperature within the mass.

We have found that optimum results are achieved in preparing coal tar primer for fully plasticized enamels if the base pitch from which the primer is to be made shows a melting point, ring and ball in glycerine, of from 190 to 240° F., advantageously at 210° F. and shows a penetration test at 77° F., according to A.S.T.M. D5–52, of from 0 to 16, advantageously at 8. The base pitch from which primer is to be made is advantageously prepared from the same crude tar that is used in making the coal tar enamels, and the high-boiling creosote oils that are used in preparing primer base are advantageously derived from the same crude coal tar that is used in the manufacture of coal tar enamel.

Example I

55 parts of plasticized coal tar enamel pitch base, prepared by mixing coal tar pitch, finely divided bituminous coal and high-boiling creosote oil and digesting the mixture at 300° C. to 315° C., was chilled to atmospheric temperature and broken into particles of about one-fourth inch maximum dimension, and charged to a ball mill containing ceramic balls. To the mill was added 45 parts by weight of volatile solvent, comprised of coal tar solvent naphtha from which the indene fraction had not been removed by washing, and with an initial boiling point of about 80° C. and with an end point of about 300° C., but advantageously boil not more than five percent at 150° C. and not less than ninety-five percent at 200° C. (Barrett's benzol method). The charge was milled at approximately 21 r.p.m. for sixteen hours at atmospheric temperature, while exercising care to prevent the charge from heating by the conversion of mechanical energy to heat. In a commercial installation of the character here under consideration, cooling means will be provided to withdraw heat from the mill and its contents at a rate equal to or exceeding the rate of heat generation within the mill.

The resulting primer, when tested in an atmospheric temperature of 72° F. and fairly high humidity, was found to be dry to the touch in twenty minutes and dry to twisting thumb pressure in fifty minutes. When tested for primer bond performance with plasticized enamels, an effective bond developed positively and a peel test procedure (conducted in accordance with A.W.W.A. standard specifications for coal-tar enamel protective coating for steel water pipe, C203–5 Sec. 2.4) at 80° F., 100° F., 120° F., 140° F. and 160° F., after heating the test plates for seventy-two hours at 160° F. and cooled to 80° F., demonstrated that a positive and acceptable bond was effected at all of the temperatures shown above.

Example II

55 parts of crushed primer base, prepared as above, and 45 parts of coal tar solvent naphtha were charged into a closed container and allowed to stand at room temperature until the coal tar solvent naphtha had effectively and resonably uniformly soaked into the crushed primer base. The resulting paste was transferred to a high speed chopping or grinding mill, the mill and its contents being suitably cooled to prevent temperature rise, and the chopping mill was operated for a few minutes until a uniform, thixotropic fluid condition of the mass was attained. Tests similar to those above outlined yielded closely similar results.

Example III

55 parts of primer base prepared as above were added to 45 parts of coal tar solvent naphtha while stirring in a Cowles disperser (U.S. Patent No. 2,351,492). The diameter of the container was set to equal three times the diameter of the disperser head, and the revolutions per minute of the disperser were set to give about 2000 to 4000 feet per minute of peripheral velocity, advantageously at 2900 feet per minute. The mixture was dispersed for approximately 40 minutes, with cooling as necessary, until the primer base had been dispersed in the vehicle and a uniform thixotropic mass resulted. Tests similar to those above yielded closely similar results.

Primer produced in accordance with each of the above-outlined procedures was placed in closed containers and stored under temperate zone atmospheric conditions. Where average temperatures of about 70° F. were maintained upon the stored primer, it was found that, after four hundred days as to Examples I and II, positive and

acceptable bond with plasticized enamels was achieved. Exposure to substantially higher temperatures, however, resulted in degradation at a more rapid rate to reduce the useful shelf life of the product. The product of Example III was chemically and physically tested and found to be substantially identical with the products of Examples I and II.

Primer produced in accordance with the present disclosure possesses other physical characteristics distinguishing it from primers for plasticized coal tar enamels heretofore known. For instance, the viscosity of the mixture (after its thixotropic "set" has been broken) is substantially unchanged within the temperature range between —20° F. and 100° F., whereas previously known primers for such enamels vary widely in viscosity in response to temperature changes.

The drying time of primer prepared in accordance with the present disclosure is virtually the same as the drying time of the selected vehicle alone, whereas primers for coal tar enamels known heretobore have, as a general rule, been characterized by greatly extended drying periods.

Many previously known primers for coal tar enamels have been characterized by a skin effect in drying, whereas it is found that primer produced in accordance with the present disclosure dries without any skin effect whatever.

When the well known "spot test" on filter paper is applied to primer produced in accordance with the present disclosure, the outer ring is uniformly light amber in color, whereas previously known primers of the character here under consideration show very dark outer rings, even when freshly produced.

We believe that the improved reliability, quick drying properties and the capacity for longer storage without significant reduction in effectiveness which are possessed by our primer are primarily, if not solely, due to the fact that our primer is a true thixotropic mixture in which the coal tar pitch base is merely dispersed and suspended in the fluent vehicle and there is no significant solution of any component of the pitch base in the fluent vehicle. So far as we are advised, such a mixture has never heretofore been prepared while maintaining the temperatures of the ingredients and of the mixture always below approximately 100° F., whereby such solution of one or more components of the pitch in the fluent vehicle, to any significant extent, is prevented and the primer base particles are not permitted to be agglutinated by the action of the primer vehicle.

We claim as our invention:

1. The process of producing a primer for plasticized coal tar enamels which comprises the steps of producing a suspension of solid particles of plasticized coal tar pitch primer base in a suitable vehicle without significant solution of pitch in the vehicle by fragmentizing solidified plasticized coal tar pitch primer base, subjecting the pitch fragments to contrition in the presence of a fluent, polar, volatile naphtha vehicle, and extracting heat from the mixture to maintain the temperature of the mixture below approximately 100° F. at all times.

2. The process of producing a primer for plasticized coal tar enamels which comprises the steps of producing a suspension of solid particles of plasticized coal tar pitch primer base in a suitable vehicle without significant solution of pitch in the vehicle by fragmentizing solidified plasticized coal tar pitch primer base, subjecting the pitch fragments to contrition in the presence of a fluent, polar, volatile naphtha vehicle, and extracting heat from the mixture to prevent the temperature at any point in the mixture from rising to the softening temperature of the pitch and from maintaining a value as high as 120° F. for as long as thirty minutes.

3. The process of producing a primer for plasticized coal tar enamels which comprises the steps of fragmentizing solidified plasticized coal tar pitch primer base, adding a liquid, polar, volatile naphtha vehicle to the fragmentized pitch in the proportion of approximately 45% of vehicle, by weight, to 55% of pitch, by weight, and subjecting the mixture to the contritional action of a discrete mass of ceramic particles while holding the temperature of the mixture below approximately 100° F. throughout the procedure, to produce a thixotropic mixture separable from said ceramic particles.

4. The process of producing a primer for plasticized coal tar enamels which comprises the steps of fragmentizing solidified plasticized coal tar pitch primer base, adding coal tar solvent naphtha to the fragmentized pitch in the proportion of approximately 45% of naphtha, by weight, to 55% of pitch, by weight, and subjecting the mixture to the contritional action of a discrete mass of ceramic particles while holding the temperature of the mixture below approximately 100° F. throughout the procedure, to produce a thixotropic mixture separable from said ceramic particles.

5. A primer for plasticized coal tar enamels consisting of a thixotropic mixture of plasticized coal tar pitch primer base with a fluent, polar, volatile naphtha vehicle.

6. A primer for plasticized coal tar enamels consisting of a thixotropic mixture of plasticized coal tar pitch primer base with a fluent, polar, volatile naphtha vehicle, said mixture being characterized by the fact that its viscosity when its thixotropic "set" is broken is substantially uniform throughout a temperature range from approximately —20° F. to approximately 100° F.

7. A primer for plasticized coal tar enamels consisting of a thixotropic mixture of plasticized coal tar pitch primer base with a fluent, polar, volatile naphtha vehicle, said mixture being characterized by the fact that substantially none of the pitch is dissolved in the vehicle.

8. A primer for plasticized coal tar enamels consisting of a thixotropic mixture of plasticized coal tar pitch primer base with a fluent, polar, volatile naphtha vehicle, said mixture being characterized by the fact that the drying time of the mixture, when spread as a coating on a surface, is substantially the same as the drying time of a similar coating of the vehicle alone.

9. A primer for plasticized coal tar enamels consisting of a thixotropic mixture of plasticized coal tar pitch primer base with a fluent, polar, volatile naphtha vehicle, said mixture being characterized by the fact that the mixture dries, when spread as a coating on a surface, substantially without skin effect.

10. The primer of claim 5 in which the vehicle is coal tar solvent naphtha.

11. A primer for plasticized coal tar enamels consisting of a thixotropic mixture of plasticized coal tar pitch primer base with a fluent, polar, volatile naphtha vehicle, characterized by the facts that its viscosity when its thixotropic "set" is broken is substantially uniform throughout a temperature range from approximately —20° F. to approximately 100° F., that substantially none of the pitch is dissolved in the vehicle, that the drying time of the mixture, when spread as a coating on a surface, is substantially the same as the drying time of a similar coating of the vehicle alone, and that the mixture dries, when spread as a coating on a surface, substantially without skin effect.

12. The primer of claim 11 in which the vehicle is coal tar solvent naphtha.

References Cited in the file of this patent

UNITED STATES PATENTS

2,228,102	Yeager	Jan. 7, 1941
2,396,910	Zaisser	Mar. 19, 1946