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ASPHALT WETTING AGENTS

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5 Claims. (Cl. 106—281)

The present invention relates to a method for producing bituminous compositions such as asphalt pavements, surfaces and linings, and in particular is concerned with improvement in the adhesivity of bituminous substances to solid aggregates of mineral origin.

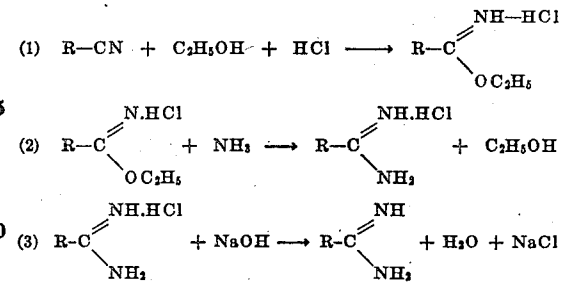
It is known that mineral aggregates such as chips, sand, rock or similar material, in a moist condition when intimately mixed with tar, petroleum pitch, mixtures of tars, solutions of petroleum pitch or other bituminous substances, cannot be properly coated by the bitumen, and if coated, the adherence of the two products to each other may be exceedingly poor. It has, therefore, been necessary in the past to carefully dry the mineral material before the preparation of the bituminous mixture. As a result, long delays in road building were occasioned by bad weather involving loss of time with corresponding mounting of costs.

It is also known that bituminous substances can be made to intimately adhere to rock aggregate by bringing the bituminous substance and the solid aggregate together in the presence of a primary or quaternary amine. While amines of this type improve the adherence of the bituminous substance to stone or rock aggregate, they are not, however, as effective when used with wet or damp road constructional materials. In particular, they suffer the shortcoming of being incapable of imparting complete adhesivity of the bituminous substance to the rock aggregates which are slightly moist or contain a substantial amount of water. Likewise, they do not effect satisfactory adherence of the bitumen to the rock or stone and the partial adherence which may be obtained is easily still further reduced, particularly by cool and damp weather. Moreover, the amines of the prior art are very difficult to synthesize from the commercial point of view since costly reduction methods must be employed in their manufacture. Also, it has been customary in the prior art to use the costly quaternary amines in the proportions ranging from 1% to 5%, these high concentrations of the active agent being necessary to obtain complete coverage of a wet aggregate.

The principal object of this invention is to provide novel means for obtaining durable bond between the above-mentioned class of rock aggregates and the bitumen binder, whether the rock aggregate is damp, wet, or dry.

Another object of this invention is to provide an inexpensive and readily available asphalt-aggregate bonding agent for purposes of road and airport construction.

According to the present invention, the above objects are accomplished by adding to a bituminous material and the like, a small quantity of an alkyl amidine which compound is obtained by the successive action of alcohol, hydrogen chloride and ammonia on a high molecular weight alkyl nitrile according to the following reactions:



R is either a saturated or unsaturated alkyl group having 10 to 23 carbon atoms to the molecule.

R may be either a saturated alkyl group of the following acids:

lauric	stearic
myristic	arachidic
palmitic	carnaubic

or an unsaturated alkyl group of the following acids:

hypogeic	linolinic
oleic	erucic
linoleic	

R may also be a substituted alkyl group such as mono- or dichloro derivatives of the above enumerated acids.

All the above indicated intermediates are inexpensive and readily available. As may be seen from the examples given below, the yields are uniformly good.

The compounds of this reaction generally termed amidines, contain the active group attached to a long chain alkyl group.

Nothing has arisen during the experimentation with and the practicing of this invention which would lead one to any other conclusion than that the broad class of compounds containing the amidine group and represented by long chain aliphatic amidines such as undecylo-amidine, lauro-amidine, myristo-amidine, palmito-amidine, stearo-amidine, oleo-amidine, lin-

olino-amidine, linoleo-amidine, and carnauboamidine will function as wetting agents for asphalt with marked effectiveness, as a result of which the asphalt will adhere more tenaciously and permanently to wet, acidic or alkaline aggregates. Of the substances enumerated as illustrative of the present invention, stearo-amidine (heptadecyl amidine) is one of the preferred species.

As a specific example of this invention stearoamidine was prepared according to the following example:

Example

(*a*) Twenty-six and a half grams of stearo nitrile, $C_{17}H_{35}CN$, was dissolved in 6.4 cc. of absolute ethyl alcohol and treated with hydrogen chloride at 30° C. until 7 grams of HCl were absorbed. The reaction was complete in less than an hour. Upon cooling, the stearo-imid-ethyl-ether hydrochloride precipitated and was recovered as a snow-white crystalline material having a melting point of 82° C. The yield obtained was quantitative. Chemical analysis showed the following results:

Analysis ---------- C=69.08, H=12.25, N=4.00
Calculated -------- C=69.06, H=12.09, N=4.08

(*b*) Twenty-eight grams of this product was dissolved in 150 cc. of absolute alcohol containing 17 grams of ammonia. The mixture was warmed on the steam bath for 15 minutes at 50° C. Upon cooling to 0° C., a crystalline precipitate was obtained which was filtered off and washed with alcohol. On recrystallization from acetone 20.5 grams of stearo-amidine hydrochloride melting at 124° C. was obtained.

(*c*) Sixteen grams of the above-described hydrochloride was dissolved in 100 cc. of absolute alcohol. To this mixture an equivalent amount of alcoholic sodium hydroxide was added. The reaction mixture was filtered hot to remove sodium chloride. On cooling the filtrate, stearoamidine was obtained as a snow-white crystalline material melting at 77° C.

Nitrogen analysis showed the following results:

Analysis:
Found ---------- N=9.37
Calculated ---------- N=9.93

In these reactions it is not necessary to isolate the intermediates. The reactor may be charged with the alkyl nitrile, the required amount of alcohol added, and hydrogen chloride passed through the mixture until the required amount of acid is absorbed. Slightly more than a mol equivalent of ethyl alcohol may be added and then ammonia bubbled through the solution until the required amount is absorbed. In commercial practice the alcohol and excess ammonia may be stripped off for recycling. The residue is treated with aqueous instead of alcoholic alkali, the water filtered off, the precipitate washed once with water and dried. Instead of filtration, the precipitate may be extracted with benzol or some other inert solvent. On removal of the solvent, the finished product is obtained as a residue and may be employed as such.

In the experiments made in evaluating the bonding properties of these organic amidines, one of the commercially available quaternary ammonia salts was selected for comparison. A quaternary ammonium salt of the type of an alkyl dimethylbenzyl ammonium chloride mixture in which the alkyl group is probably the fatty alcohol residue resulting from cocoanut oil reduction to corresponding alcohols, which is one of the efficient asphalt bonding agents on the market under the trade name of "Triton K-60" was employed.

As a specific example, a Venezuelan rapid curing cutback asphalt was prepared according to the following formula:

	Parts per cent
Heavy naphtha having a boiling range of 200–450° F	25
Asphalt (90 penetration at 77° F.)	75

The bonding agents of the present invention may be advantageously incorporated with the asphalt blend either by dissolving 0.1% to 1% (based on the asphalt) of the agent in one of the customary solvents such as naphtha, kerosene, tar oils, etc., and thoroughly mixing such solution with the heated asphalt or tar (about 200° F.) or by stirring the agent (an alkyl amidine) directly with the asphalt blend and heating the mixture to a temperature of about 150° F. for one-half to one hour.

Sixteen samples of the rapid curing cut-back asphalt were prepared as above described. The sixteen samples were then divided into two groups of eight for tests with the alkyl amidine and quaternary ammonium salt respectively. Each group was classified with respect to concentration. The concentration being 0.2% and 0.4% of the agents used based on the rapid curing cutback asphalt. In each group, four samples were applied to dry rock and four samples applied to wet rock.

The application of the asphalt compositions was effected by thoroughly mixing with the rock aggregate and curing one set of samples for one hour and the other set of samples for two hours at 140° F. The results obtained are shown in the following table:

Table

[Stripping resistance test]

In Venezuelan rapid curing cut-back asphalt	Dry rock		Wet rock (2% H_2O)		
	1 hr. cure	2 hr. cure	Mixing ability	1 hr. cure	2 hr. cure
0.2% stearo amidine	100	100	95	70	85
0.4% stearo amidine	100	100	100	95	100
0.2% quaternary ammonium salt	70	85	75	15	40
0.4% quaternary ammonium salt	95	100	90	25	-----

In the above table, the term "stripping resistance" is defined as the percentage of the aggregate surface still remaining coated with asphalt, after the coated mixture which has been cured for one hour at room temperature has been covered with water maintained at room temperature for a period of 20 hours.

As may be seen from the data, both blends cure well with dry rock as would be expected. With wet rock, however, where the need for superior bonding agents arises, the superiority of the amidine blend is pronounced. Hence, it is apparent that the bonding agents of the present invention exhibit desirable characteristics by showing a marked improvement in the stripping resistance test. By the present invention, road making is greatly simplified because the hitherto expensive bonding agents can be dispensed with and effective result obtained by using smaller quantities of less expensive alkyl amidines.

While reference has been made particularly to

the treatment of asphalt, it will be understood that the principles disclosed are applicable to any equivalent bituminous material whether natural or artificial and solutions thereof in light and heavy distillate and residual oils, coal tar, coal tar pitch and its solutions, shale oils or mixtures of these substances. Similarly, the present invention can be applied in the preparation of asphalt containing surface coating compositions such as are employed in coating iron pipes and concrete walls.

Numerous other modifications of the invention may be made, for example, by adding the alkyl amidines in admixture with free fatty acids to asphalt in order to obtain improved adhesivity upon alkaline rock aggregate.

While the preferred embodiment of this invention has been disclosed, it will be readily apparent to those skilled in the art that many changes and variations may be made therein without departing from the spirit of the invention. It is, therefore, my intention to claim all novelty inherent in the invention as broadly as the prior art permits.

I claim:

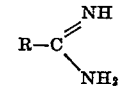
1. An improved bituminous bonding material comprising a bituminous material, a solid mineral aggregate and 0.1% to 1.0% of a long chain alkyl amidine the alkyl group having from 10 to 23 carbon atoms to the molecule.

2. A composition of matter comprising a rapid curing cut-back asphalt, a solid rock aggregate and ranging from 0.1% to 1% of stearo-amidine.

3. A composition of matter comprising a rapid curing cut-back asphalt, a solid rock aggregate and ranging from 0.1% to 1% of oleo-amidine.

4. A composition of matter comprising a rapid curing cut-back asphalt, a solid rock aggregate and ranging from 0.1% to 1% of linoleo-amidine.

5. An improved bituminous bonding composition comprising a bituminous material, a solid mineral aggregate and 0.1% to 1.0% of an alkyl amidine, represented by the formula



in which R stands for a member of the group consisting of a saturated and an unsaturated alkyl group having 10 to 23 carbon atoms inclusive.

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