Progress with Adhesion-Improving Bitumen Additives

ANDREJS ZVEJNIEKS, Chemical Division, General Mills, Inc., Kankakee, Ill.

Some theoretical aspects of adhesion are discussed and the test methods for testing adhesiveness of bituminous binders are reviewed. An attempt is also made to summarize and compare the current practices with bitumen additives in the United States and in Europe. A coordinated large-scale road test program is suggested in order to keep up with the recent European development.

Where bituminous binders are used, many problems and failures are caused by water. It has been demonstrated experimentally that the tensile strength of a hot-mix pavement can be lowered to one-fourth of its original value by soaking in water for four days. Adhesion-improving bitumen additives are used to avoid and overcome these failures. Generally these additives consist of polar molecules, which tend to concentrate in the interfaces, adhere to the aggregate surfaces, and strongly improve the bond between the binder and the aggregate. For cold-mixed pavements and seal coats, an active adhesion is required; that is, the additive-improved bitumen must have the ability to adhere to wet aggregates and to replace water on wet surfaces.

Reliable test methods are of prime importance for evaluation and classifying of adhesion-improving additives. The test methods used can be described as measurement of fundamental physio-chemical properties, and simulation of road conditions.

Usage of adhesion-improving bitumen additives in some European countries seems to be far ahead of the corresponding usage in the United States. In Western Europe additives are used much more frequently and at higher levels. Extensive tests in Sweden and England have resulted in acceptance of amine-type additives. The latest trend is essentially toward new applications for improved bituminous materials.

The limited heat stability of additives known to be really efficient and economical does not allow heating of "doped" bitumens for prolonged periods. European practice is to mix additives and cut-back asphalt directly in the distributors. Additives in solid form are often preferred, owing to easier and safer handling.

● THE PRINCIPLE of improving the properties of a cheap basic material with additives is successfully used throughout industry. For instance, modern lubricating oils are "built" to such an extent that some authorities regard the base oil as being only a carrier for different types of additives.

For the road building industry where bituminous binders are used, many problems and failures are caused by water. Special bitumen additives are used to overcome these problems and failures.

At present stage of development, the usage of asphalt adhesion-improving additives in some European countries, particularly in Sweden, England, France and West-Germany, is far ahead of the usage in the U.S. For instance, asphalt consumption for road building in Sweden was about 0.7 percent of the asphalt consumption in the U.S. (45,000 vs 6,000,000 tons in 1955). For this same period, the usage of additives in Sweden was approximately equal to the total usage of additives in the U.S.

The aggregate has a greater affinity for wager than for bitumen, therefore, a wet aggregate cannot be successfully mixed with an unimproved binder. Thermodynamic considerations show that energy is gained when water replaces bitumen on the aggregate surface, and stripping is likely to occur in areas exposed to water. Nevertheless, apparent stripping is only part of the problem. It has been demonstrated experimentally, using a test method similar to U.S. Public Roads Administration immersion compression test, that the tensile strength of a "hot mix" type pavement can be lowered to one-forth of it's original value by soaking in water for four days, even if no visible stripping occurs. Figures 1a and 1b present tensile strength curves of two mixes—one with and the other one without additive. The relative tensile strength t, defined as:

$$t = \frac{\text{tensile strength of wet slabs at 2.5 mm extension} \cdot 100}{\text{tensile strength of dry slabs at 2.5 mm extension}}$$

is 26 percent without additives compared with 81 percent with additives. This, as well as many other observations, illustrates that the static immersion-stripping tests and the nomenclature anti-stripping agents are inadequate. The term adhesion-improving additives is proposed and used in this paper.

BASIC THEORIES

The author considers the adhesion between aggregate and bitumen to be constituted as shown in Figure 2a. Polar molecules present are adsorbed by the aggregate and by the colloidal asphaltene particles. The lipophilic parts of these adsorbed molecules are solubilized by the non-polar part of the bitumen. As mentioned, water has a greater affinity for the aggregate surfaces, and the polar molecules found in natural bitumens are not adsorbed strongly enough to withstand water. After soaking in water these organic molecules are replaced by the water as shown in Figure 2b.

Adhesion-improving additives are chemicals which are especially well adapted to assist and improve the action of compounds already found in natural bitumen. The primary requirements for an adhesion-improving additive are:

1. To be efficient when present in small amounts;
2. To be economical;
3. To give an adhesion which is able to withstand the aggresion of water (passive adhesion); and
4. To have no undesirable side effects on the binder.

Moreover, for all types of cold mixed pavements and seal coats, an active adhesion is required; that is, the additive—improved bitumen must have the ability to adhere to wet aggregate and to replace water on wet aggregate and on wet road surfaces.

There are two basic interpretations of the function of adhesion-improving additives in the road building industry. The opinion which was predominant until the late forties, regarded the additives as an insurance against failures caused by unforeseen circumstances. The more recent opinion realizes that, with adhesion-improving additives, the properties of the bitumen can be changed to such an extent, that a material with principally new properties and new potential uses is obtained. This improved bitumen often enables the use of cheaper construction and can be used in fields where a conventional bitumen fails.

METHODS OF TESTING

The full benefits of bitumen additives can not be utilized without satisfactory test methods and without intelligent specifications. Particularly due to the great cost of road construction work, reliable test results are required to decide why, where, which and how much of the adhesion-improving additives are to be used. In practice, there are too many variations in the test methods and in the test results as well.

Having no possibilities to determine which additive is the most efficient and the most economical one, contractors are forced to use the cheapest one.

In order to check the adhesion, an old contractor in the author's old country used to chew a piece of asphalt. The one which stuck to his teeth was a good one. More modern test methods which are used for testing of bituminous binders on aggregate surfaces for adhesiveness and for resistance against water can be divided in two main classes, as follows:

1. Measuring of fundamental physio-chemical properties.
2. Methods simulating road conditions.

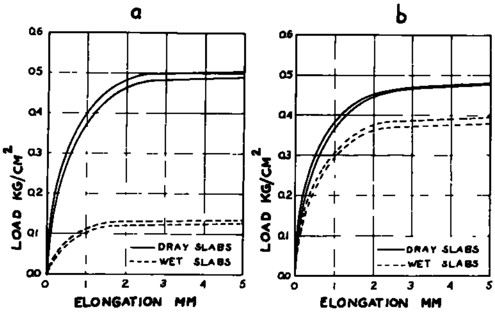

Figure 1. Tensile strength curves for (a) test slabs made of binder without additives, (b) test slabs made of binder containing 1 percent octadecyle amine.

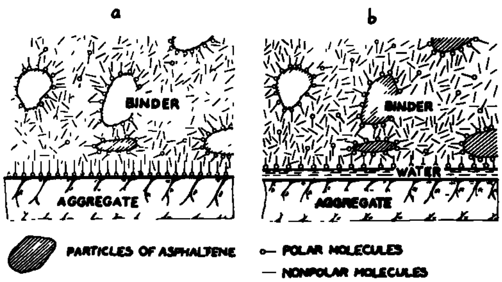

Figure 2. Adsorption of polar oil molecules to the particles of asphaltene and aggregate, (b) the same binder and aggregate after soaking in water.

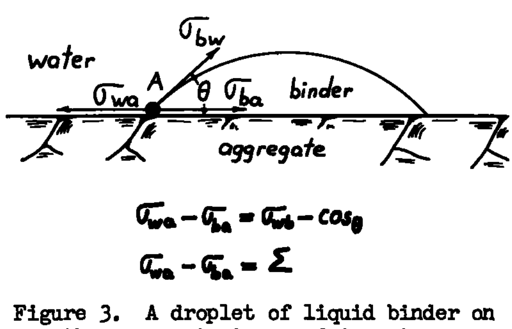

Figure 3. A droplet of liquid binder on the aggregate immersed in water.

MEASURING OF PHYSIO-CHEMICAL PROPERTIES

Of the simple physio-chemical properties connected with adhesion in the presence of water, the interfacial tension between binder and water (which is numerically equal to the interfacial energy) and the adhesion tension are very important. These two properties have been measured and used successfully as an indication of the type and strength of adhesion. The conception of adhesion tension, Σ, is explained in Figure 3, representing a droplet of liquid binder on the aggregate immersed in water.

Any point A on the solid surface which lies on the dividing line between the two liquids is a junction for three forces—interfacial tensions. By an unbalance of these three forces, point A has to move along the surface of the aggregate, the aggregate being a solid. The condition for A being in balance is:

$$\sigma_{wa} \quad \sigma_{ba} = \sigma_{wb} \cos\theta$$

where:

σ_{wa} = the interfacial tension between water and aggregate,

σ_{ba} = the interfacial tension between binder and aggregate,

σ_{wb} = the interfacial tension between water and binder,

θ = the contact angle.

The expression σ_{wa} and σ_{ba} is symbolized by Σ and is called the adhesion tension. At present, it is not possible to determine σ_{wa} and σ_{ba} separately, whereas Σ can be measured according to Bartell (2) in his cell, or according to Hallberg (3) in his adhesion meters.

Some complications are caused by hysteresis. The hysteresis known for the contact angles is observed also for adhesion tension. Hallberg solves this problem by measuring two limit values,

$$\Sigma_b = \Sigma_{binder} \text{ and } \Sigma_w = \Sigma_{water},$$

as follows:

1. $\Sigma_b = \Sigma_{binder}$ = the adhesion tension of the binder on an aggregate is the maximum resistance in dynes per cm which the binder is capable of withstanding when exposed to water under pressure. This value of adhesion tension corresponds to the receding contact angle for the binder:

$$\Sigma_b = \sigma_{wb} \cos\theta_{receding}$$

ERRATA

BULLETIN 192

In Bulletin 192, the formula on page 28 should read:

$$\sigma_{wa} - \sigma_{ba} = \sigma_{wb} \cos \theta$$

and the first line of the following paragraph should read:

The expression $\sigma_{wa} - \sigma_{ba}$ ....

2. $\Sigma_w = \Sigma_{water}$ = the adhesion tension of the water on an aggregate is the maximum resistance in dynes per cm which the water is capable of withstanding when exposed to binder under pressure. This value of adhesion tension corresponds to advancing contact angle for the binder (receding for water):

$$\Sigma_w = \sigma_{wb} \quad \cos\theta \quad \text{advancing}$$

Typical Σ_b and Σ_w curves as functions of concentration of the additive (octadecyl amine) are shown in Figure 4.

Both Σ_b and $-\Sigma_w$ are negative for unimproved binder, which means that binder can be displaced by water without the aid of exterior forces. At an amine concentration of about 0.05 percent, Σ_b becomes positive, which means that water cannot replace binder without the help of exterior force. This condition is called passive adhesion. At an amine concentration of about 1.0 percent, the Σ_b is 12 cyn/cm, which means an exterior force of 12 dyn/cm is necessary to displace binder with water. At this concentration, $-\Sigma_w$ also becomes positive, which means that the binder is able to adhere to wet aggregate and to displace water spontaneously from the aggregate surface. This condition is called active adhesion.

METHODS SIMULATING ROAD CONDITIONS

The methods in this category start from the static immersion-stripping tests and stretch through more ellaborate stability tests, to "road machines" and full scale road tests. Immersion-stripping tests have the advantage of being simple and fast. Nevertheless, these tests are inadequate for the more thorough investigations because of the poor reproducibility of results and also because the trends obtained often are not in agreement with the actual performance of the material on the road.

For definite answers to all of the questions connected with the economical usage of adhesion-improving additives, advanced tests in road laboratories as well as full scale tests are necessary.

Figure 5 shows a photograph of the "road machine" built and used at the Swedish State Road Institute, Stockholm.

In this apparatus (4), the traffic speed and load on the test pavement which was laid on a circular track could be varied within ranges to duplicate the speeds and loads of commercial vehicles. The test pavement could also be exposed to artificial rain and the temperature in the test room could be lowered below the freezing point. Among the numerous test results obtained with this apparatus, the one concerning seal coats and reported by Hallberg at the 9th Road Congress, Lisbon, 1951, could be of particular interest. Hallberg states (5); "A surface treatment with M_C-5 without additives was quite free of chippings after 800 wheel passages when subjected to heavy traffic in rain immediately after laying, whereas a surface treatment tested in the same way, but with 1.5 percent amine in the cut-back, was still, after 50,000 wheel passages, practically without defects."

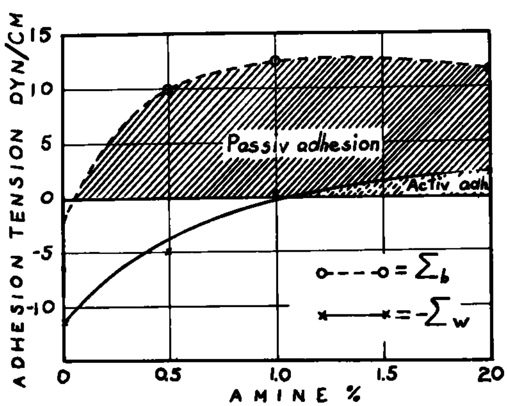

Figure 4. Adhesion tension—concentration curves for octadecyl amine in cut-back (MC - 0).

Figure 6 (7), is a reproduction of a photo taken of a maintenance seal coated Swedish highway showing a rather sharp dividing line between a section using cut-back containing 1.5 percent amine (in foreground) and a section using the same cut-back but without addi-

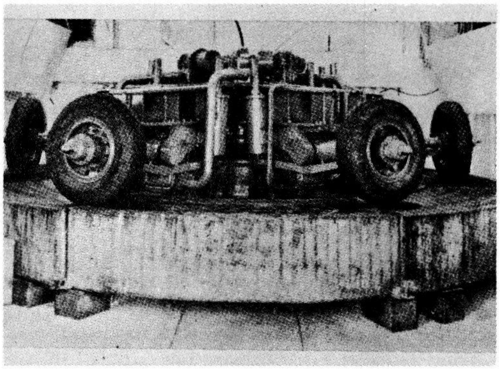

Figure 5. Road machine of Swedish State Road Institute.

tive (in background). These seal coatings were made in good weather. Heavy rainfall occurred 3 days after laying.

CHEMICALS USED

The number of chemicals proposed for use as adhesion-improving additives to bitumen or for treating of aggregate is very large. These are often marketed under imaginative synonyms and trade names. For an intelligent evaluation, it would be desirable, or perhaps even necessary, if the chemical composition or equivalent information concerning the additives were made known and stated along with the publication of the test results. Classes of compounds which, to the author's knowledge, are most widely used as adhesion-improving additives in commercial road construction are: primary fatty amines, fatty amino amides and imidazolines, fatty diamines, fatty acids, fatty acid-amine mixtures, and metal soaps. Also, alkynolamine fatty esters, secondary and tertiary fatty amines, rosin amines, quarternary ammonium compounds, fatty alcohols, and silicones have been proposed and used.

The heat stability of additives is often considered to be critical. Unfortunately, all of the additives known to be really efficient cannot withstand heating for prolonged periods. As a rule, for best results the chemicals have to be added to the bitumen the same day as it is to be used. Some progress has been made in development of more heat-stable adhesion-improving additives which can be added to the asphalt at the manufacturing stage. Nevertheless, the original efficiency of the heat-stable additives seems to be much lower.

PROGRESS IN THE UNITED STATES

The present U. S. road building program is at an all-time high and demands tremendous quantities of materials, labor and equipment. However, it seems that the adhesion-improving bitumen additives have not yet found their proper place in this program. Some states and also some private companies and contractors are using addivites enthusiastically, while the others are more or less indifferent toward the use of additives.

One of the reasons why the use of additives is still a questionable matter is that, in too many cases, insufficient amount of active ingredient is used. The adhesion at low concentrations of additive is only "passive" and, therefore, is often inadequate for severe conditions. A concentration in excess of 0.5 percent, and often even in excess of 1.0 percent of the active chemical is required to obtain "active adhesion," Some failures could also originate in the numerous and different types of aggregate. There are additives which are efficient only on some particular types of aggregate.

Many types of adhesion-improving chemicals are used in this country, none being especially predominate.

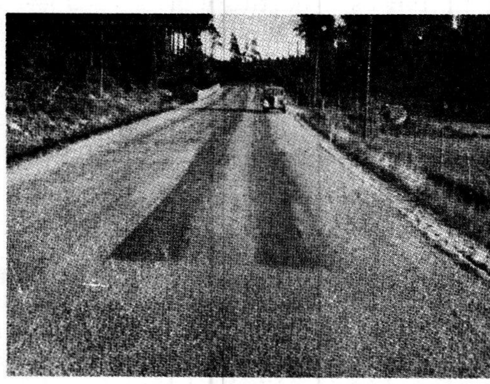

Figure 6. A maintenance seal coat on a Swedish road with cut-back (MC - 5) containing 1.5 percent amine (in foreground) and the same seal coat but without amine (in background). Seal coating was made in good weather—heavy rainfall three days later.

The major consumption is in cheaper types of pavements for secondary roads. The trend is to incorporate additives in the asphalt at the manufacturing stage, therefore, it has been suggested that the heat stability is of critical importance. Some promising work has been done in developing heat-stable adhesion-improving additives, nevertheless, heat stability requirements which are too hard, eliminate all the classes of compounds currently known to be really efficient and economical. For this reason, some compromise has to be made between the heat stability requirements and the other desirable properties. Particularly owing to the simplicity with which the additives can be added to the cut-back directly into the distributors, the same day the cut-back is used, the requests for absolute heat stability could be given some new considerations.

Rapidly increasing interest in the amine type additives for asphalt emulsions is occuring.

PROGRESS IN EUROPE

In Sweden the use of primary fatty amines as adhesion-improving additives to bitumen broke its way through dur ng the years 1951-1953. This caused revolutionary changes in paving technology and during these years consumption of cut-back asphalt in Sweden increased 15 fold. Seal coatings, then on decline, made a strong come back and are now used not only on secondary roads, but also on heavily traveled highways.

The development in England has been a very similar one. The English authorities Lee and Nicollas stated in a paper presented at a conference held in London in 1952 (6): "Surface dressing carried out in the unsettled weather often experienced in Great Britain can be a hazardous technique, and in the wetter areas of the country much money has been lost in poor seasons. This has been the position until recently; now a reliable solution of these troubles has been found."

In England, amine type additives are also used successfully in tar surfacings and with limestone chippings.

In general, the European practice is to purchase asphalt or cut-back and the additive separately, making the mixing in the distributor tanks and shortly before the use. Additives in solid form are often preferred owing to easier and safer handling.

A new promising line of development in Sweden, made possible through the use of efficient adhesion-improving additives, is low cost secondary roads of gravel and residue oils. These roads require very little maintenance and can be regraded after about one year's service without addition of new material. Additives are also used to some extent in "hot mixes," particularly for thin carpets and for open textured asphaltic concrete.

SUMMARY

For the road building industry, where bituminous binders are used, many problems and failures are caused by water. It has been demonstrated experimentally that the tensile strength of a "hot mix" type pavement can be lowered to one-fourth of its original value by soaking in water for four days. Adhesion-improving bitumen additives are used to avoid and overcome the failures.

For cold mixed pavements and seal coats, an active adhesion is required; i.e., the additive-improved bitumen must have the ability to adhere to wet aggregate and to replace water on wet surfaces.

Usage of asphalt adhesion-improving additives in some European countries seems to be far ahead of the corresponding usage in the United States. Extensive tests under varying, and sometimes very hard service conditions, have been run in Sweden and in England. The result of these tests was that during the years 1951 to 1953 amine type additives broke their way through definitely.

The limited heat stability of additives which are known as being really efficient and economical does not allow heating of prepared asphalts for prolonged periods. European practice is to mix additives and cut-back asphalt directly in the distributors. Additives in solid form are often preferred owing to easier and safer handling.

The author feels that adhesion-improving additives are here to stay and that European practice could be of some value also in the United States.

DISCUSSION

Being at an early stage of development bitumen adhesion improving additives could solve many problems and have a great future. The fields to be conquered first are seal coats and all other types of "cold mix" and "road mix." Grouting techniques using improved bituminous materials could be of particular interest for highway base course stabilization.

More test data is badly needed before the right chemicals and the right methods can be prescribed and sanctioned for each individual case. For the best results, laboratory investigations will have to be coordinated with full scale road tests and certain correlations between laboratory results and actual performance will have to be established.

The author feels that the facts accumulated justify a large scale U.S. road test program, planned and carried out by the cooperative efforts of the road authorities and industries involved. This program should have mutual advantages and be of nationwide value.

Last but not least, essentially new applications for improved bituminous materials might be possible or even probable.

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