The Effect of the Physical and Chemical Characteristics of the Aggregate on Bonding

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Executive Summary

This literature review discusses the primary physical and chemical characteristics of aggregates that have a significant effect on the bonding between aggregate and asphalt. Specifically, the report examines how morphology, electrical properties, and mineral composition of aggregate affect the aggregate's interaction with water. The report also examines how these aggregate properties affect stripping. Although the report focuses mainly on aggregate surface parameters and general aggregate properties, the report also considers the chemical functionalities in both asphalt and aggregates that play a predominant role in bonding, as well as the effects of surface modification of the aggregate and the use of antistripping agents.

The report discusses the mechanisms of stripping, the dependence of asphalt-aggregate bond strength on aggregate characteristics, the effect of asphalt absorption by aggregates on stripping, methods for determining the mineral composition of aggregates, environmental and processing conditions that affect the aggregate's physical state, and the composition and function of antistripping agents for bituminous surfacings.

The study concludes that there is little research data on the effects of the numerous variables and parameters that influence bonding, and mentions that existing tests and techniques that quantify these properties are often complicated and/or expensive.

Analysis of the information in the review has led to the formulation of a research plan to investigate some of the more important, but less understood, aspects of aggregate physical and chemical properties that control bonding:

1) Characterization of aggregates--compositional, morphological, and other physical properties. Herein some physical techniques could be used to determine the relationship between these properties and bonding.

2) Characterization of aggregate in terms of electrokinetic properties and determination of the importance of these properties to bonding.

3)   Interaction between water and the aggregate surface. Herein the kinetics of dissolution of surface constituents and the resulting interactive surface chemistry could be studied.

4)   Surface modifiers and additives--the effects of direct application of additives to aggregate surfaces on the properties of aggregate active sites, dissolution behavior, kinetic effects, asphalt bonding energy and type, properties of asphalt, electrokinetic properties, and absorption properties could be investigated.

An important avenue recommended for further research is the pretreatment of aggregates. A study of direct application of additives to aggregate surfaces on the properties of aggregates could lead to important commercial developments.

OBJECTIVE

The overall objective of this document is to review the literature pertaining to the primary physical and chemical characteristics of aggregates that have a significant effect on the bonding between the aggregate and the asphalt. Specific areas of focus include the role played by morphology, electrical properties, and mineral composition of the aggregate in its interaction with water and consequently on stripping.

The review also deals with the chemical functionalities in both asphalt and aggregates that play a predominant role in bonding, as well as the effect of surface modification of the aggregate and use of anti-stripping agents.

In conclusion, based on a critical analysis of the reviewed material, a research plan is proposed to investigate some of the more important but less understood aspects of aggregate physical and chemical properties that control bonding.

INTRODUCTION

The physical and chemical characteristics of the aggregate are believed to be a significant factor in determing the strength of the asphalt-aggregate bond (1). This literature review attempts to elucidate the important factors that influence this bond strength and consequently stripping. The emphasis is on aggregate surface parameters and general aggregate properties.

The review begins with an overview of the different mechanisms of stripping, or asphalt-aggregate bond failure, with emphasis given to the role aggregate characteristics have in these mechanisms. This is followed by a concise summary of the dependence of asphalt-aggregate bond strength on fundamental aggregate characteristics. The objective of this portion of the literature review is to identify aggregate characteristics which play a dominant role in asphalt/aggregate bonding or debonding.

In addition to aggregate surface texture, aggregate porosity and pore structure are also known to affect stripping. Aggregate properties that affect porosity and some of the correlations between aggregate pore parameters and asphalt absorption are also summarized in this review.

The review also provides an overview of the different analytical techniques used in elemental analysis of the aggregates. The emphasis is on X-ray diffraction, since it is the most widely used technique that provides reliable data. The basic working principle for this technique and some of the more recent modifications are included herein.

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Apart from "intrinsic" aggregate surface properties, environmental and processing conditions in the mix plant can significantly alter the physical state of the aggregate surface, and, in turn, can affect the asphalt-aggregate bond strength. The changes that may occur in the aggregate physical state are identified, and their possible influence on stripping is mentioned in this review.

Finally, the review addresses the usage of antistripping additives (ASA) as adhesion promoters. In addition to some of the salient features of ASA, the heat stability of amine based additives is also reviewed. The application of other, more recent ASA is also included herein.

MECHANISMS OF STRIPPING

A general definition of stripping is "the breaking of the adhesive bond between the aggregate surface and the asphalt cement" in an asphaltic pavement or mixture (1). Stripping is a complex problem dependent on many variables, including the type and use of a mix, asphalt characteristics, aggregate characteristics, environment, traffic, construction practice, and the use of anti-strip additives. However, the presence of moisture at the aggregate/asphalt interface is a common factor to all stripping related problem (2).

A bituminous mixture derives its strength from the cohesional resistance of the binder and grain interlock and frictional resistance of the aggregate. The cohesional resistance is only fully available if a good bond exists between the binder and the aggregate (3). If a good bond exists, failure of the mixture occurs within the binder (3). If the bond is poor, the failure may occur at the binder-aggregate interface and may result in premature failure of the mix.

A review of the literature indicates that there may be as many as five different mechanisms by which stripping of asphalt from an aggregate surface may occur (4). These five mechanisms include detachment, displacement, spontaneous emulsification, pore pressure, and hydraulic scouring. It appears that these mechanisms may act individually or together to cause adhesion failure in bituminous mixtures. A brief description of each of the suggested mechanisms of stripping follows.

Detachment

Detachment is the separation of an asphalt film from an aggregate surface by a thin layer of water, with no obvious break in the asphalt film (1,3). Where stripping by detachment has occurred, the asphalt film can be peeled cleanly from the aggregate, indicating a complete loss of adhesion (1). The theory of interfacial energy provides the rationale for explaining the detachment mechanism. This widely accepted theory considers adhesion as a thermodynamic phenomenon related to the surface energies of the materials involved,

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namely, asphalt and mineral aggregates. The surface tension of water is much lower than that of asphalt. The wettability of an aggregate increases as the surface tension (or free surface energy) of the adhesive decreases *(3)*.

Thus, if a three-phase interface consisting of aggregate, asphalt, and water exists, water reduces the free surface energy of the system more than does asphalt to form a thermodynamically stable condition of minimum surface energy *(3)*. The theory of interfacial energy emphasizes the effect of polarity of the molecules present at the surface of the two phases. Most aggregates have electrically charged surfaces. Asphalt, which is composed chiefly of high molecular weight hydrocarbons, exhibits little polar activity; therefore, the bond that develops between asphalt and an aggregate is primarily due to relatively weak dispersion forces *(5)*. Water molecules, on the other hand, are highly polar and are attracted to aggregates by much stronger orientation forces *(5)*.

Displacement

Stripping by displacement results from the penetration of water to the aggregate surface through a break in the asphalt film *(1,3,6,7)*. The break can be caused by incomplete coating of the aggregate initially or by film rupture *(1,3,5,6)*. Because the asphalt film at these locations is generally thinner and under tension, rupture of the asphalt film is probably at the sharp edges and corners of angular aggregate pieces as a result of traffic loading. Stripping by displacement can result from pinholes in the asphalt film, which can form soon after coating a dusty aggregate *(6)*. The concept of stripping by displacement is congruent with the thermodynamic approach to adhesion; that is, water will displace asphalt from an aggregate surface when the three-phase interface exists.

The chemical reaction theory of adhesion can also be used to explain stripping by displacement *(7)*. Changes in the pH of the microscopic water accumulations at the mineral aggregate surface can alter the type of polar groups adsorbed, as well as their state of ionization/dissociation, leading to the build-up of opposing, negatively-charged, electrical double layers on the aggregate and asphalt surfaces *(7)*. The drive to reach equilibrium attracts more water and leads to physical separation of the asphalt from the aggregate *(7)*.

Spontaneous Emulsification

In spontaneous emulsification, water and asphalt combine to form an inverted emulsion, where asphalt represents the continuous phase and water represents the discontinuous phase. The formation of such an emulsion leads to stripping and is further aggravated by the presence of emulsifiers such as mineral clays and some asphalt additives *(1,6,7)*.

Fromm observed that spontaneous emulsification occurs whenever asphalt films are immersed in water but that the rate of emulsion formation depends on the nature of the

asphalt and the presence of additives *(6)*. The fact that stripping has been observed to be reversible lends support to the spontaneous emulsification mechanism because evaporation of the water from the emulsion would restore the asphalt to its original condition *(6)*.

Pore Pressure

Pore pressure has been suggested as a mechanism of stripping in high void mixes where water may circulate freely through interconnected voids *(1,3)*. Upon densification of the mix from traffic loading, water may become trapped in impermeable voids that previously permitted water circulation. Further traffic may induce high excess pore pressures in the trapped water causing stripping of the asphalt film from the aggregate *(1,3)*.

Hydraulic Scouring

Hydraulic scouring is a mechanism of stripping that is applicable only to surface courses. Stripping due to hydraulic scouring results from the action of vehicle tires on a saturated pavement surface. This causes water to be pressed down into the pavement in front of the tire and immediately sucked away from the pavement behind the tire. This compression-tension cycle is believed to contribute to the stripping of the asphalt film from the aggregate (1).

In addition to the mechanisms outlined above, which have gained varying degrees of acceptance among investigators of the stripping problem, other potential mechanisms for stripping have been proposed. Osmosis has been suggested as a possible mechanism of stripping, but no laboratory evidence for this mechanism has been found *(6)*. It has been observed that asphalt will creep up an air-water interface, such as an air bubble on the pavement surface, as a result of surface tension *(6)*. If the air-water interface is sufficiently large, this pulling of the asphalt film may result in film rupture or may result in a film that is so thin that spontaneous emulsification is rapid *(6)*.

Related to the mechanism of stripping is the initiation and progression of stripping in a typical asphalt pavement. Inspection of field specimens of stripped pavements has revealed that stripping begins at the bottom of the layer and works its way up, stripping mostly the coarse aggregate *(1,6)*. This behavior is not surprising because the asphalt at the bottom of a pavement layer is in tension upon the applications of load and is often subject to prolonged exposure to moisture from water trapped within a granular base course above the subgrade.

As stated in the beginning of this review section, asphalt pavement stripping is a complex problem related to a large number of variables. Those variables, which have been identified through years of study of the stripping problem, can be grouped for purposes of discussion into six categories: type and use of mix, asphalt characteristics, aggregate characteristics,

environment, traffic, and construction practice *(4)*. This review is primarily concerned with the dependence of asphalt-aggregate bonding on aggregate characteristics.

DEPENDENCE OF ASPHALT-AGGREGATE BOND STRENGTH ON AGGREGATE CHARACTERISTICS

The mineralogical and chemical composition of an aggregate is known to be an important factor in the susceptibility of an asphalt pavement to stripping. The mineralogical and chemical composition of an aggregate influences its surface energy and its chemical reactivity; it also accounts for the presence of adsorbed coatings on the aggregate surface *(11)*. With regard to their affinity for water, aggregates are typically classified as being either hydrophilic (water loving) or hydrophobic (water hating). Hydrophilic aggregates are considered to be acidic with regard to their chemical nature and generally exhibit a high silica content. Hydrophobic aggregates, on the other hand, are considered to be chemically basic and exhibit a low silica content. Carbonate rocks, such as limestone, produce hydrophobic aggregates.

It is generally observed that hydrophobic aggregates have a higher resistance to stripping of asphalt films than do hydrophilic aggregates; however, acidic quartzite has been shown to be less susceptible to stripping than most basic aggregates *(3)*. Furthermore, stripping has been observed in mixes containing limestone aggregate, which is often considered to be immune to stripping *(14)*. It is generally concluded then, that few, if any, aggregates can completely resist the stripping action of water.

The physical characteristics of an aggregate surface have been shown to be somewhat related to the occurrence of stripping in asphalt pavements. The surface texture of an aggregate affects its coatability, in that, it is easier to coat a smooth aggregate surface than it is a rough one *(3,11)*. A complete initial coating of aggregate pieces is obviously necessary to minimize the destructive effect of moisture on a bitumen-aggregate bond.

When an aggregate is coated with asphalt, the asphalt penetrates the pores and cracks of the aggregate surface to some extent *(12)*. It is, therefore, felt that an aggregate that has a porous, slightly rough surface will promote adhesion by providing for a mechanical interlock between the bitumen and the surface of the aggregate *(3,11)*. Aggregates that have large pores on their exposed surfaces, such as limestone, appear to exhibit stronger bonds with asphalt than do aggregates that have fewer or smaller surface pores such as quartz *(12)*.

Laboratory tests indicate that stripping is more severe when angular aggregates are used *(9)*. This phenomenon is believed to be related to the increased potential for film rupture provided by angular aggregates.

Sometimes a newly crushed aggregate when used in an asphalt paving mixture exhibits a poor stripping resistance as compared to the same aggregate after it has been stockpiled

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(or aged) for some period of time *(1)*. It is a characteristic of many aggregates that one or more layers of water molecules become strongly adsorbed on the aggregate surface with exposure as a result of electro-chemical attractions. Upon aging, the outermost adsorbed water molecules may become partially replaced or covered by organic contaminants present in air, such as fatty acids and oils, and this reduces the stripping potential of the aggregate *(12)*. This contamination process, along with general oxidation, reduces the free radicals, and reactive sites, on the aggregate surface and is believed to be the reason why an aged or weathered aggregate has a higher stripping resistance than one that is freshly crushed *(12)*.

Adsorbed coatings are often present on the surface of aggregates, and the nature of the adsorbed coatings present on a given aggregate is related to its mineralogical and chemical composition. A partial list of substances that have been encountered on the surface of aggregates includes clay, silt, calcium carbonate, iron oxides, opal, gypsum, manganiferous substances, soluble phosphates, dust from crushing, ferruginous coatings (on gravel), oil, fatty acids, oxygen, and water *(11)*. Of these coatings, clay, silt, dust from crushing, and water have been found to be detrimental with regard to the susceptibility of an aggregate to stripping; whereas ferruginous coatings, oil, and fatty acids have been found to beneficial *(11)*.

Aggregates that have a dry surface adhere better to asphalt and have a higher stripping resistance than do damp or wet aggregates *(3,9)*. Heating aggregates that contain free water and adsorbed water films, under conditions permitting vapor to be driven off, remove the free water and the outermost adsorbed water molecules, causing the interfacial tension between the asphalt and the aggregate surface to decrease *(3,12)*. This results in a decrease in the stripping potential of the aggregate binder interface. It has also been observed that asphalt adheres better to hot, as opposed to cold, aggregate--probably due to deeper penetration (or absorption) of asphalt into aggregate pores--and this stronger adherence generally results in a stronger bond *(3,12)*.

EFFECT OF ASPHALT ABSORPTION BY AGGREGATE ON STRIPPING

Absorption of asphalt by paving aggregates is one factor that can have serious repercussions on the asphalt-aggregate bond. Many studies have attempted to correlate aggregate physical and chemical properties to absorption of asphalt.

The loss of asphalt by absorption can be substantial with many aggregates. Not long ago bituminous engineers faced the problem of mixes being too dry on the pavement because of the absorption of bituminous materials by aggregates. These mixes had been designed according to a surface-area-formula, void filling concept, or by precedence. If selective absorption occurs, the asphalt may change its physical, rheological, and chemical properties to such an extent that it may behave differently as a film than it does in the bulk phase as is indicated by physical and chemical tests run on the asphalt alone.

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Aggregate absorption may result from any combination of the following reasons (all may lead to failure of the paving mixture)*(31)*:

1. Incorrectly calculated percent voids, percent voids filled with bitumen, or voids in the compacted mineral aggregate (CMA). Since one or more of these voids properties is being used as criteria for the design of paving mixtures, an incorrect voids calculation may result in mixtures lacking durability or future stability.

2. A thin asphalt film, making the mix more susceptible to stress and weathering.

3. Not enough binder, rendering the mix more susceptible to water action.

4. A change of physical and chemical properties of the asphalt film. (This usually causes low temperature cracking of the asphalt pavement.)

Some of the frequently used techniques for evaluating absorption-related aggregate properties are briefly described below.

1. Total porosity: Total porosity is a measure of the total pore volume in the aggregate and can be calculated from measurements of the powder and bulk densities of all of the coarse aggregate fractions. The powder density can be determined using a pycnometer. Total aggregate porosity is calculated using the following equation:

$$\text{Total porosity, per cent} = 100 - \frac{\text{Bulk density}}{\text{Powder density}} \times 100.$$

The bulk aggregate density is estimated using a standard ASTM method (ASTM C127-59).

2. Effective porosity: Effective porosity is a measure of the volume of permeable, or interconnected pores in an aggregate. It can be estimated using a mercury porosimeter. In so doing, the effective pore volume is taken as the volume of mercury that can be injected into the aggregate at a high pressure (e.g. 2000 psia). And the bulk volume is taken as that occupied by the aggregate submerged in mercury at a low pressure, e.g. of 5 psia. And the effective porosity is estimated as the ratio of the effective pore volume (or the volume of assumed interconnected permeable pores having a pore entry radius range from 21.32 to 0.05 microns), to the total bulk volume of the aggregate. The effective porosity is usually expressed as a percentage.

3. Water permeable or 24-hour soaked porosity: The water permeable porosity is estimated by multiplying the percent of water absorption into an aggregate by the bulk specific gravity of the aggregate. Both of these measured are measured using the standard 24-hour aggregate soaking procedure (ASTM C127-59).

Aggregate Pore-Size Distribution

Aggregate pore size distribution is one of the most important properties in mix design, but it is difficult to determine. Knowledge of pore space characteristics is important because of their direct influence on other physical and chemical properties *(22)*. For concrete aggregates, pore characteristics determine the flow of moisture into and out of an aggregate, its water retentivity, and the development of pressure during a freeze-thaw cycle, which relates directly to concrete durability. For aggregates in asphaltic mixtures, the pore size distribution may determine both the amount and mechanism of absorption *(11)*.

The importance of pore-size distribution in concrete aggregates has been realized and studied extensively *(15-21)*. However, there has been relatively little published data with regard to the pore-size characteristics of asphalt aggregates and their relationship to the absorption and other behavior of asphaltic mixtures.

The pore-size distribution of aggregate particles can be measured by forcing mercury under pressure into the evacuated pores of the solids, as state earlier, using an apparatus described by Purcell *(22)*, now generally referred to as the mercury porosimeter.

The equation describing the penetration of mercury into pores under pressure is given by *(20)*:

$$pr = - 2s \cos \theta \qquad (1)$$

where p is the pressure applied, r the pore radius, s the surface tension of mercury, and θ the contact angle of the mercury with respect to the solids.

The derivation of the equation and the operation of the apparatus are described in references *(20,22,23)*.

Absorption by CKE and Oil Methods

A number of investigators have attempted to evaluate aggregate absorption with kerosene and to correct for the amount of asphalt absorbed by aggregates in mixture design. In 1942, Hveem *(26)* introduced his Centrifuge Kerosene Equivalent (CKE) test. The CKE is the quantity of kerosene absorbed by 100 g of aggregate under a specific set of conditions of soaking and centrifuging. It has been shown to be a function of the surface area and the absorptive capacity of an aggregate. It is used as part of the design procedure for bituminous mixtures outlined in Hveem's Method *(27)*. Lohn *(28)*, using a method similar to that proposed by Hveem, was able to correlate bitumen absorption of an aggregate with kerosene absorption. He also studied the effects of saturation time, centrifuge, time, and centrifuge force or kerosene retention. He finally adopted a test procedure in which the weight of the aggregate saturated with kerosene is used. The aggregate is saturated with kerosene by soaking it in kerosene while centrifuging at a force of 400 times gravity.

Donaldson et al. *(29)* proposed some modifications to Hveem's CKE method, namely increasing the soaking time to 30 minutes and testing a nonabsorptive aggregate of the same gradation for purposes of baseline comparison. It is believed by many that kerosene is a more representative absorption agent than water for evaluating asphalt binders because it has wetting properties that are more similar to those of asphalt than does water *(28,30)*.

Correlations Among Aggregate Pore Parameters, Water Absorption and Asphalt Absorption

In general, water absorption is assumed to be indicative of the potential of an aggregate to absorb asphalt. Aggregates having a high water absorption are more likely to absorb asphalt than those having a low water absorption. Direct determinations of asphalt absorption by the aggregate and asphalt to be used are preferred to indirect prediction from water absorption data *(31)*.

The equilibrium amount of asphalt absorption is usually about 50 percent to 80 percent of that of water absorption, depending on how the amounts of asphalt and water absorption are measured *(31)*.

CKE, Oil, and Asphalt Absorption

Definite linear relations have been reported between kerosene and asphalt absorptions for the aggregates studied *(31)*.

Porosity and Asphalt Absorption

The basic reason for aggregate absorption is the existence of pores in the aggregate. Total porosity, pore size distribution, and continuity of the pores are believed to determine the nature and degree of absorption.

The water permeable porosity is about 80 percent of the total porosity. The mercury penetration porosity is slightly lower than the water permeable (24 hour) porosity. A linear relationship has been reported between asphalt absorption and porosity *(31)*.

Pore Size and Asphalt Absorption

It is generally accepted that not all pores of an aggregate are of the same size; nor, do all aggregates have the same pore-size distribution. It is felt that there could be a pore-size range (or ranges) that is optimum for asphalt absorption.

The following conclusions have been drawn for pore-size and absorption correlations by D.Y. Lee *(31)*:

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1. Porosity in a pore-size range larger than 0.5 micron has a direct effect on asphalt absorption. Absorption varies linearly with porosity in this pore-size range.

2. No relations could be established between microsize pores (less than 0.1 microns) and bitumen absorption.

Chemical Composition and Porosity

Aggregate dolomitization appears to be accompanied by increases in both porosity and pore size according to Murray (32). That is, for high dolomite aggregates, the higher the dolomite content, the more porous the aggregate is likely to be. The relation between dolomite content of a carbonate aggregate and its absorptive capacity can be deduced as: an aggregate with a high dolomite content is more likely to be absorptive than one with a low dolomite content.

DETERMINATION OF MINERAL COMPOSITION

The principal mineral components of aggregates are usually reported in terms of their percent calcite content, and percent dolomite content. These are usually measured via EDTA, supplemented by X-ray diffraction analyses. The experimental procedure generally used in performing an EDTA titration is that described by Bisque (25), with a few minor modifications.

Techniques Used to Perform Elemental Analysis of Aggregates

High precision bulk elemental analyses of rocks and minerals can be accomplished by wavelength dispersive X-Ray Fluorescence Spectroscopy (XRF). The basic working principle of this technique is described below (25).

When an atom is irradiated with a sufficiently high energy source, an inner-shell (usually a K or L shell) electron is ejected leaving the atom in an excited energy state. This excited energy state is not stable, and, to return to its stable ground state, a deexcitation process occurs. The vacancy created by the emission of an inner-shell electron from an atom is filled by an electron previously residing at a higher energy level. The excess energy resulting from the transition often is dissipated as electromagnetic radiation of sufficiently high energy to be called an X-ray photon. The advantages of the XRF method are (33):

1. X-ray emission spectrum is simple and orderly;

2. X-ray spectra are relatively independent of chemical state;

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3. X-ray excitation and absorption vary uniformly with atomic number;

4. Absorption and enhancement effects are predictable;

5. Spectral line interference is relatively infrequent;

6. Sample preparation can be nondestructive;

7. Specimen form can be solid, powder, paste, liquid, or gas;

8. High precision and accuracy can be attained;

9. Sample preparation and analysis times can be relatively fast and are not usually labor intensive.

The disadvantages of the XRF method are:

1. Sensitivity for low atomic number elements is frequently poor;

2. Sensitivity for low abundance levels (below parts per million) is poor without preconcentration procedures;

3. Interelement effects within the sample must be recognized and corrected;

4. Standards are required;

5. Initial cost of equipment is relatively high.

XRF is capable of determining 10 major elements, namely, Na, Mg, Al, Si, P, K, Ca, Ti, Mn, and Fe in rocks and minerals. Concentrations of the metals are determined independent of the oxidation state. The elements are reported in the oxidation state in which they most commonly occur in the earth's crust.

In the XRF method, there are two principal sources of short-term imprecision. The first is the instability of the instrument and the second is the imprecision of the sample preparation (33). A refined fusion X-ray fluorescence technique has been described by B. P. Fabbi in American Mineralogist (Vol. 57, pp 237-245, 1972). Fabbi used an XRF fusion technique for the determination of SiO_2, Al_2O_3, total Fe (as Fe_2O_3), MgO, CaO, K_2O, TiO_2, P_2O_5 and MnO in silicate rocks. He fused the sample with $LiBO_2$ and then ground and pelletized the fused bead prior to X-ray irradiation. This procedure eliminated most of the matrix problems associated with X-ray fluorescence analysis. Values obtained by this method compared favorably with the preferred chemical values.

ENVIRONMENTAL AND PROCESSING CONDITIONS WHICH AFFECT THE AGGREGATE PHYSICAL STATE

The nature of an aggregate surface to which asphalt is to adhere is the first item to be considered in determining the formation and permanence of an asphalt-aggregate bond (12).

Aggregates in general are composed of atomic lattices, in which each atom is bound to the aggregates around it through coordination bonds of an electron nature. If an aggregate is cleaved, the atoms at the new surfaces are bereft of some of their neighbors, and hence some of their coordination bonds are broken. These atoms then seek to form new bonds to replace the old, broken ones. New coordination bonds can be formed in two ways (13):

1. In some cases, the coordination forces that are originally directed outward from the surface tend to turn around and conjugate with internal atoms in the aggregate. This is accompanied by a distortion of the crystal lattice as the surface atoms are pulled closer to the internal atoms, or

2. Water, oil and other contaminants in the air are attracted to the fresh surface.

If all the coordination forces were directed inward, the aggregate would have no affinity for asphalt or other externally-applied materials. This, as far as is known, never happens, and all freshly cleaved aggregates do have an absorbed surface layer, or film, to varying degrees.

The most common adsorbed film is water, since water vapor is always present when rocks are cleaved in air. At room temperature, it takes only a few minutes for a rock to adsorb the equivalent of several molecular layers of water (17). Spreading occurs spontaneously, in accordance with the Second Law of Thermodynamics, when it decreases the free energy of the system (12).

Asphalts and other organic compounds which are insoluble and non-reactive with water spread over a water surface in air; the rate at which they spread depends largely upon their viscosity. The rapid spreading of oil on water is an example; this spreading continues until the oil film is so thin that it exhibits interference colors (50-200 molecules thick).

Although the destruction by water of asphalt films on an aggregate occurs under various conditions, and by several mechanisms, it most likely occurs when there is a discontinuity, and there is a line of juncture where asphalt, free water and stone are all in contact.

Usually asphalt and normal organic materials voluntarily spread over water films on an aggregate surface and also tend to be stripped from these films by water. The rate at which these processes occur depend somewhat on the magnitude of the free energy evolved (ΔF), but in practice probably is controlled chiefly by viscosity of the asphalt (39).

Preheating of the Aggregate

When an aggregate surface that is covered with an adsorbed water film is heated under such conditions that water vapor can escape, it loses its outermost adsorbed water molecules. This causes the interfacial tension of asphalt to decrease when it is in contact with the hot aggregate surface. For such reasons, asphalt applied to a hot aggregate surface is bound much more strongly than when it is applied to a cold aggregate surface (12).

In general, a hot mix asphalt concrete is usually resistant to stripping if during its preparation the aggregate was preheated before the bitumen was applied such that water vapor was driven off of its surface.

Weathering of Aggregate

At least one important effect of weathering on aggregate properties is predictable from surface energy considerations. As an aggregate ages and is exposed to cycles of varying temperature and humidity, its outermost adsorbed water molecules are partially replaced or covered by organic contamination (e.g. by fatty acids) from the air. This reduces the spreading coefficient and also the stripping coefficient for the aggregate surface (40).

The reduction of the stripping coefficient may be very significant, and is thought to be the primary reason why weathered aggregate is considered in practice to be superior to freshly cleaved stone in macadam and sheet paving.

Aggregate stored in a refinery has been observed to resist stripping better than freshly cleaved rock. The stored aggregate apparently adsorbs oils from the atmosphere (12).

Effect of Dust on Stone Surfaces on Stripping

Dust on aggregate surfaces has a tendency to trap air when the road oils or cutbacks are applied. This weakens the asphalt/aggregate bonding, or joint, by preventing intimate contact between the aggregate and the bitumen. It also promotes stripping by creating channels at the interface, through which water can penetrate. The importance of these effects in practice is not known, but theoretically, at least, they could be significant. If this is the case, washing freshly crushed aggregate to remove dust particles should be beneficial (43).

ANTISTRIPPING AGENTS FOR BITUMINOUS SURFACINGS

Adhesion of bitumen to aggregate is a surface phenomenon and depends on close contact of the two materials and the mutual attraction of their surfaces.

Aggregates are more or less hydrophilic (water-loving), which means that they are easily coated by water. Bitumen is hydrophobic, i.e. has no attraction for water (water-hating). On the other hand, most aggregates can also be attracted by bitumen (44). If the aggregate surface is covered by a thin film of water, the bitumen may cover the aggregate particle readily but it will not stick to its surface unless the bitumen replaces the water film. Bitumen may also cover dust-coated aggregates without sticking to them. The dust layer prevents contact of the bitumen film with the aggregate surface.

For the closest possible contact between bitumen and an aggregate surface, the bitumen must be liquefied - either by heating, by emulsifying, or by blending with petroleum solvents. The ability of a liquefied bitumen to make close contact with aggregate surfaces is called "wetting power". The wetting power of bitumen is largely controlled by its viscosity. All other properties being the same, the lower the viscosity of an asphalt the greater the wetting power of the asphalt (45).

Bitumen is a hydrocarbon product and has a rather low surface tension, much lower than water. This means water will wet aggregates more easily than bitumen and that water can displace bitumen that has covered a dry aggregate.

In order to have a good bond between binder and aggregate the nature of the aggregate surface must be changed. The surface tension should be decreased so that the aggregate becomes more lipophilic (oil-loving) (45).

Aggregates are sometimes classified as alkaline or acidic, the alkaline types being limestone and marble and the acidic types being granite and quartzite. This type of aggregate classification is somewhat simplified as all aggregates contain a mixture of both alkaline and acid minerals. An important factor to the adhesion properties of an aggregate is its content of silica, SiO_2.

It has been generally observed that, alkaline aggregates such as limestone (which have a low silica content) give good adhesion to bitumen. This can be explained by the fact that bitumen (particularly those of Venezuelan origin) contain naphthenic acids (46). The naphthenic acids have a carboxylic acid group, COOH, and a hydrocarbon part which is similar in structure to the bitumen itself. When such a molecule comes in contact with an alkaline aggregate, the carboxylic acid part will be absorbed on the surface with the hydrocarbon part pointing outward. This will change the surface of the aggregate enough to enable the binder to adhere to it even if water should be present.

A major disadvantage with aggregates such as limestone is that they normally get polished under traffic action and should therefore be avoided in surface courses.

Siliceous aggregates are normally not so sensitive to polishing but have another disadvantage. Being acidic, they do not respond to the action of the naphthenic acids in the bitumen. In fact, the acids counteract each other and a good bond between a siliceous

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aggregate and bitumen is difficult to obtain. Sometimes there are also alkaline components in the binder but they are very weak and cannot give a good bond to silica *(45)*.

Surface texture, porosity and absorption properties of aggregates also affect the adhesion to bitumen, as was discussed earlier. Smooth-surfaced aggregates will not hold a bitumen film as well as rough-surfaced aggregates. Porous particles that absorb bitumen will hold the film better than smooth-surfaced ones.

The resistance to water of a mixture made with a moisture-sensitive aggregate may be improved by treating the aggregate, treating the asphalt, or changing the mixture design. The addition of antistripping additives to the asphalt is routinely specified by many agencies. For maximum effectiveness, these additives must be attached to the particular aggregate being used; moreover, their effectiveness has been found to vary with the asphalt source *(35)* and the pH of the water present. Some additives have improved moisture resistance in the laboratory; however, similar improvements have not always been obtained in the field *(36)*. This may be attributable to the heat stability of the additives or may reflect the inadequacy of present laboratory test procedures. In some instances, antistripping additives have been found to change the physical properties of asphalt cements and to greatly decrease in effectiveness with heating (ASTM D1574) *(37,38)*.

Additives applied directly to the aggregate surface may also improve the moisture resistance of some asphalt-aggregate mixtures. Heavy metal ions dissolved in a sodium oleate solution and added to the aggregate have been shown to improve the wettability of asphalt on aggregate surfaces *(39)*. Fromm *(40)* determined that heavy metal cations, when applied to aggregate surfaces, could improve moisture resistance. Ferric naphthenate was found to be particularly effective. Sodium dichromate has also been shown to be effective when added to the aggregate in an aqueous solution.

The effectiveness of hydrated lime for improving the resistance of certain asphalt mixtures has been known for many years. Hydrated lime is often added as a mineral filler, but it is more effective as an antistripping additive if it is added as a slurry and allowed to cure for several days. Recent research suggests that the hydrated lime absorbs carboxylic acids in the asphalt, which results in a more water-resistant asphalt-aggregate bond *(40)*. Hydrated lime has also been found to change the mechanical properties of asphalt mixtures *(42)*.

Active and Passive Adhesion

If an antistripping agent is added to the bitumen, even wet aggregate surfaces may be coated. This is defined as active adhesion.

If the bitumen does not have the power to coat wet aggregate, but has coated, dry aggregate and the contact angle between water, aggregate and bitumen does not change when immersed in water, it is defined as passive adhesion.

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In practice it is possible to coat dry surfaces with bitumen, but stripping may occur at a later stage due to the influence of water, although the stripping process can be relatively slow, e.g. with very high viscosity bitumen. In such circumstances the addition of a stable amount of anti-stripping agent gives added protection by passive adhesion. The level of additive required in this case is lower than when coating wet aggregate surfaces, for which active adhesion is required (47).

COMPOSITION AND FUNCTION OF ANTISTRIPPING AGENTS

Antistripping agents are normally based on fatty amines, which are surface active compounds. There are also other types of agents which are based on amidoamines and imidazolines.

Fatty Amines

The amines having a long hydrocarbon chain are the most suitable antistripping agent for bitumen. They are called fatty amines, since they are produced from fatty acids.

In the presence of water or acid, the amine is ionized to give an amine ion, $R\text{-}NH_3$, which has a positive charge; thus fatty amines are cation active (cationic).

The physical properties of fatty amines depends on the length and nature of the hydrocarbon chain. The shorter the chain, the lower the melting point. Unsaturated hydrocarbon chains give lower melting points than saturated ones.

The chemical properties of fatty amines can be varied by changing the number of amine groups and their positions in the molecule (48).

The balance between the length of the hydrocarbon chain and the number of amine groups has a great influence on the adhesion power. Short hydrocarbon chains are less soluble in bitumen than longer ones as their bond with the bitumen is weaker. Optimum performance is obtained with 14-18 carbon chains amines, with one or especially two amine groups, one of which is a primary amine group (48).

Function of Amine Based Antistripping Agent

When small amounts of fatty amine are added to bitumen, the bitumen is able to wet hydrophilic aggregate surfaces, since the additives have the ability to change the surface properties of aggregates.

Fatty amines form a strong, sometimes even a permanent chemical bond with silica. This can withstand the action of water and significantly improve the adhesion between bitumen

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and aggregate *(47)*.

The amines consist of a long chain hydrocarbon and amine group. The amine group reacts with the aggregate surface, and the hydrocarbon portion, which is hydrophobic, is directed into the binder. The net effect is that the long hydrocarbon chain acts as a bridge between the hydrophilic aggregate and hydrophobic bitumen surfaces thus, encouraging a strong bond between them.

Solid and Liquid Antistripping Agents

An amine based on fatty acids with equal length of the hydrocarbon chain can be either solid or liquid at a certain temperature. This difference in physical appearance does not affect the adhesion power. Liquid and solid antistripping agent of fatty amine type can replace each other in all applications at the same dosage level.

Liquid antistripping agents are preferred in applications where the binder is used at temperatures below the melting point of solid adhesion agent (~50°C). They are also preferred when automatic dosage pump systems are used. On the other hand, when the antistripping agent is added manually to the binder, the solid type is preferred with respect to the handling safety.

Heat Stable Antistripping Agents

Bitumen contains varying amounts of acidic components which can react with fatty amines. These reactions proceed very slowly at temperatures below 100°C but are accelerated at higher temperatures; eventually reaching the stage where no improvement in adhesion power is detectable. In hot bitumen, the initial reaction between fatty amine and bitumen results in the formation of salts which are still active as antistripping agents; this does not influence the overall efficiency provided they remain unchanged *(49)*. However, prolonged storage leads to further reactions producing inert compounds showing no adhesion properties. At 120°C, 50 percent of the added amine may be inactivated in 24 hours and at 180°C all the amine can be stored only for a few hours before losing its activity. This limitation on the use of fatty amines is important to recognize. The amine itself can, however, be stored at ambient temperatures indefinitely without a loss in efficiency.

Iron Naphthenate

The second class of anti-strip agent is iron naphthenate, which is an iron salt of naphthenic acids. Naphthenic acids are a mixture of carboxylic acids obtained from the alkali washes of petroleum fractions. Their copper salts have been used in wood preservatives and their lead, manganese, zinc and iron salts are used as oxidation catalyst

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(i.e., driers) for paints and varnishes.

It has been presumed that iron naphthenate operates as an antistrip agent by migrating to the aggregate-asphalt interface (while the asphalt is still hot) and forming a water-resistant complex *(50)*. Complaints of an unpleasant smell associated with the product have been attributed to the solvent being used as a carrier rather than to the iron oxidation catalyst in paint to promote drying.

Hydrated Lime

The third class of anti-strip agent is hydrated lime or calcium hydroxide *(51)*. Applied as a slurry pretreatment of aggregate prior to mixing, the calcium hydroxide serves to consolidate fines and clays on the aggregate surface and to provide calcium binding sites for asphalt on the aggregate surface.

There is considerable evidence that acids in asphalt migrate to the asphalt-aggregate surface. These acids form salts with the sodium and potassium minerals frequently associated with stripping-prone aggregate. The sodium and potassium salts are much more water soluble than are the calcium salts of the same acids. Hence, lime slurry treatment of aggregate results in the formation of calcium salts at the asphalt-aggregate interface, giving a material that is more resistant to water-stripping.

CONCLUSIONS

Although this review identifies some of the more important physical and chemical properties of aggregates that play a critical role on the bond between asphalt and aggregate, it also draws attention to the numerous variables and parameters that influence bonding and the paucity of research data concerning their effect on bonding. Further, although tests and techniques which quantify these physical and chemical properties exist, they are often complicated and/or necessitate expensive equipment. Development of simple, yet reliable tests to predict the aggregate performance (as regards to water susceptibility) could provide for challenging future research work.

Although published research data concerning aggregate pretreatment is scarce, this concept opens a whole new avenue for further concentrated work. A variety of pretreatment compounds along with pretreatment conditions that work in an effective and feasible manner could be investigated.

Based on an analysis of the aforementioned review some of the anticipated areas for focused research concerning this field might include:

a. Characterization of Aggregates - Compositional, Morphological, and Other

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Physical Properties. Herein, simple physical techniques could be used to determine the relationship between these properties and bonding.

b. Characterizing aggregate in terms of electrokinetic properties and determining the importance of these properties to bonding.

c. Interactions Between Water and the Aggregate Surface - Herein, the kinetics of dissolution of surface constituents and the resulting interactive surface chemistry could be studied.

d. Surface Modifiers and Additives - the effect of direct application of additives to aggregate surfaces on the properties of aggregate active sites, dissolution behavior, asphalt bonding energy and type, electrokinetic properties and adsorption properties could be investigated.

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