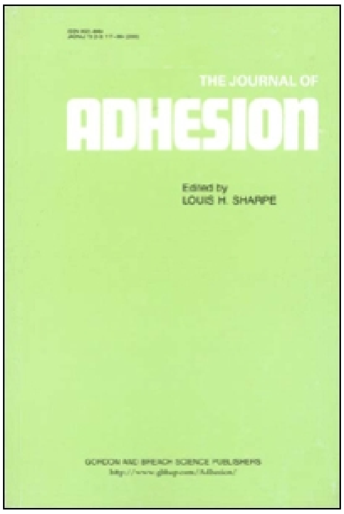

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Ferric Oxide Adhesion Promoters for Water Resistant Asphalt Pavements

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Additives are often necessary to prevent the loss of strength of asphalt paving materials when they are exposed to moisture. It has been known for many years that naturally-occurring aggregates which contain iron oxides are resistant to the phenomenon of water stripping in asphalt pavements. In this investigation Pyrex brand glass was chosen as a model substrate for silicate-type aggregates in order to determine the effect of iron compounds on the adhesion of bitumen to glass in the presence of water. It was found that both iron naphthenate and iron oxide were equally effective in maintaining adhesion in the presence of moisture. Two independent methods were employed to measure the wet adhesion-peel testing and contact angle measurements. Both methods confirmed that iron is an essential element for prolonged retention of wet strength adhesion. It is postulated that iron oxides react with acidic components in asphalt to form organometallic complexes which subsequently bind to the glass surface and form strong attachments which are resistant to hydrolysis. Iron compounds were equally effective with other substrates such as limestone and traprock, indicating equally good performance with other types of aggregates. Calcium additives in the form of lime did not confer wet adhesion. It is suggested that the known effectiveness of lime as an antistripping agent may be attributed to other factors such as reaction with polar groups in the asphalt, rendering it less hydrophilic. A boiling water test is described for assessing whether a particular asphalt mix may be susceptible to eventual loss of interfacial adhesion when exposed to water.

Keywords: Antistripping agents; asphalt pavements; roads; bitumen; coupling agents; aggregates; water damage; moisture resistance; adhesion; iron; iron oxide; ferric oxide

INTRODUCTION

Most asphalt paving mixtures are moisture sensitive and when exposed to water for long periods of time will lose strength and become more susceptible to the phenomenon of "stripping" and stress cracking. A recent review of the problems of water damage to asphalt paving materials has been published by Ruth [1]. This study shows that the problem is pervasive and is particularly severe in areas where freezing temperatures and moisture are present. The water damage is accelerated by multiple cycles of freezing and thawing [2]. The phenomenon of stripping is associated with adhesive failure at the aggregate-asphalt interface and is usually the first stage leading to crack formation and raveling. Asphalt binders are relatively hydrophobic but will become plasticized as moisture diffuses into and permeates the bulk of the material. The major loss of strength occurs at the asphalt-aggregate interface due to preferential hydration of the inorganic surfaces. This is not surprising since the very high surface energies of inorganic aggregates compared with those of asphaltic materials ensure that the work of adhesion will eventually become zero in the presence of water. The addition of lime or other antistripping agent may only provide temporary relief from this type of failure. Calcium oxide or hydrated lime are not always satisfactory for the prevention of water stripping and a more reliable additive would be desirable. Organic amines are also used for this purpose despite their toxicity. These cationic adhesion promoters can sometimes accelerate moisture attack after an initial delay [1]. According to Maupin [3], "*Stripping has always been an elusive phenomenon. The incorporation of additives seems to help, but stripping still occurs for no explainable reason*".

Various theories of adhesion have been proposed which include preferential adsorption of polar species, mechanical interlocking, and surface energy concepts [4]. This paper addresses the somewhat unique ability of iron compounds to resist adhesion loss at bitumen-inorganic interfaces in the presence of water.

It has been previously observed that aggregates which contain iron oxides confer exceptional water resistance to asphalt paving materials [5]. In 1974, Fromm [6, 24] showed that iron naphthenates were effective antistripping agents for asphalt mixtures containing limestone, silica, glass, trap rock and granite type aggregates. However, during paving trials the strong odour of iron naphthenate was found to be objectionable and the method was aborted. Subsequent investigations at the University of Toronto around 1980 confirmed the findings of Fromm and found that iron oxide was equally effective for the purpose of maintaining adhesion in the presence of water [7–9]. The iron oxide treatment is less costly, non toxic, environmentally safe and does not impart an offensive odour. Although the mechanism of adhesion has not been proven, it is believed that the iron oxide forms complex adducts with certain acidic components in the heated asphalt and that these complexes then become chemically attached to the surfaces of the aggregate. This is illustrated in Figure 1. The nature of the transition metal bond resists hydration and maintains the integrity of the asphalt-aggregate bond in the presence of water. This type of interaction may account for the exceptional antistripping properties of naturally-occurring aggregates which contain iron oxides. Since iron oxides are major by-products of steel manufacturing, the oxide is both plentiful and relatively inexpensive for this application.

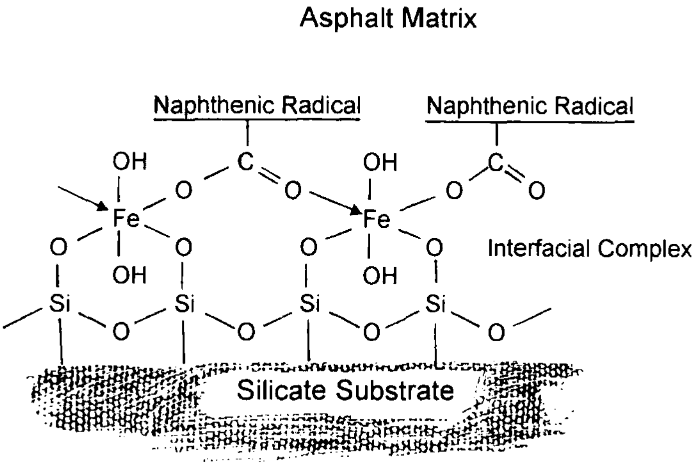

FIGURE 1 Schematic representation of the interfacial bond between ferric naphthenate and a silicate surface. The coordinate iron complex forms a hydrolysis-resistant interface with the silicate.

THEORY OF ADHESION

The physical attraction between an asphalt binder and an aggregate surface is governed by the surface energies of the respective materials. The surface energy of a material may be represented by a dispersive (non polar) component and a polar component (which may include ionic attraction and hydrogen bonding) [10]. The interfacial tension, γ_{AB}, between two materials A and B may be represented by Eq. (1) below.

$$\gamma_{AB} = \gamma_A + \gamma_B - 2\left[\gamma_A^d \gamma_B^d\right]^{1/2} - 2\left[\gamma_A^p \gamma_B^p\right]^{1/2} \tag{1}$$

here the subscripts A and B refer to the aggregate (A) and bitumen (B), respectively. The interfacial surface energy, γ_{AB}, is the sum of the aggregate surface energy, γ_A, and the bitumen surface energy, γ_B, minus the geometric means of the individual dispersive (d) and polar (p) surface energies of the two materials A and B. A measure of the attraction between the two surfaces is the reversible work of adhesion, W_{adh}, which is given by

$$W_{\text{adh}} = \gamma_A + \gamma_B - \gamma_A\gamma_B = 2\left[\left(\gamma_A^d \gamma_B^d\right)^{1/2} + \left(\gamma_A^p \gamma_B^p\right)^{1/2}\right] \tag{2}$$

Under dry conditions the work of adhesion is always positive but in practise it is important to know if the work of adhesion remains positive in the presence of moisture. Since the surface energy of water (in air at 25°C) is 72 mJ/m^2 it will spontaneously displace bitumen (the surface energy of which is near 33 mJ/m^2 [11]) from any aggregate when it reaches equilibrium. Therefore, the work of adhesion, W_{adh}, is zero in the presence of water for virtually all types of inorganic surfaces [9]. If the interface A-B is immersed in water until equilibrium is obtained then the work of adhesion becomes

$$W_{\text{adh}} = \gamma_{AW} + \gamma_{BW} - \gamma_A\gamma_B \tag{3}$$

where the interfacial energies are now γ_{AW} and γ_{BW} in the presence of water (W). Application of Eqs. (2) and (3) will show that the work of adhesion will be negative i.e. effectively zero, when physical (i.e. secondary) bonds are involved [9]. Asphalt has a surface energy of approximately 33 mJ/m^2 [11] whereas most inorganic aggregates will have surface energies (when dry) exceeding 100 mJ/m^2 [12, 13]. The much greater surface energies of inorganic surfaces in general will tend to adsorb water preferentially at the interface until they are in equilibrium with their surroundings. Since the diffusion rate of water in asphalt is relatively slow, it may require several months for a pavement to reach equilibrium with atmospheric humidity and soil moisture after it is laid. Under high humidity conditions it is expected that complete separation of the asphalt from the aggregate will occur as the water diffuses into the composite.

Plastics engineers have known for many years that silane coupling agents are usually essential in order to maintain positive filler adhesion in polymer composites (containing inorganic filters) in the presence of moisture. Silane coupling agents are also necessary to prevent the loss of adhesion of epoxy resin adhesives on inorganic substrates in humid environments. Since the surface energy of bitumen is near that of most polymers, similar behaviour in the presence of moisture is expected. In order to maintain adhesion in the presence of water it is necessary to develop chemical bonds which cannot be displaced by water. Since silane coupling agents are obviously too costly for this purpose, alternative cost-effective solutions are needed to preserve the integrity of asphalt concrete under moist conditions.

Since physical bonds (polar, hydrogen bonding, dispersive) are readily displaced by water, the question becomes what other types of interfacial attachments can be considered that are not affected by moisture? Ionic bonds are strong but are often susceptible to hydrolysis with corresponding loss of adhesion. Hydrated lime (calcium hydroxide) is frequently employed as an antistripping agent although it exhibits poor adhesive properties in the presence of water. The favorable wet strength retention with this additive is probably due to other factors such as neutralization of the polar acidic components of asphalt. This reaction reduces the water sensitivity of the binder and increases its strength and modulus.

One solution is to employ a type of covalent bonding which is not susceptible to hydrolysis such as organometallic complexes or metal chelates. Chromium complexes have been used commercially for promoting the adhesion of glass fibers to polyester resins [14]. Quilol$^{\text{TM}}$ and Volan$^{\text{TM}}$ [15] were two of the earliest commercial organometallic sizing agents for glass fibers. These transition metal complexes can form strong, hydrolysis-resistant bonds between organic molecules and inorganic surfaces when exposed to water. Since iron and chromium are closely related transition metals, iron complexes are potential coupling agents for promoting adhesion in asphalt composites. Brown-colored aggregates containing iron oxides have been known to impart water resistance to asphalt pavements [5]. Other authors have identified amine complexes of transition metals (copper) as superior adhesion promoters for wet strength retention [2]. Calcium oxides or lime sometimes contain iron oxides which can increase the wet strength retention of asphalt mixes [16].

Naphthenic acids are obtained from the alkali extraction of petroleum. They are complex mixtures of branched, linear, cycloaliphatic, and naphthenic (alicyclic) acids. Metal naphthenates are prepared by directly heating metal oxides or metals at about 100°C for 4 to 12 hours with naphthenic acids until the metal is completely solubilized. Iron begins to show catalytic activity at temperatures above 66°C. Iron naphthenates are commonly used as catalysts in alkyd coatings where they accelerate the curing process. Calcium salts are sometimes used as promoters in these curing reactions. Since iron naphthenate is soluble in asphalt it is convenient for studying the effect of iron concentration on surface adhesion. Iron oxides are also effective adhesion promoters although it is suspected that the iron oxide first reacts *in situ* with acidic components in the heated asphalt to form iron soluble salts. Increasing the acidity of asphalt by air oxidation or maleation will increase its reactivity towards iron oxide and basic oxides.

EXPERIMENTAL

Pyrex brand borosilicate glass plates (7.5 cm × 15 cm) were selected as model inorganic substrates. The composition of the glass is shown in Table I. Glass is representative of silica or silicate-type minerals.

The asphalt binder was Shell Venezualan (pen 85/100) typically used for hot mix paving in the metro Toronto area. The properties of this asphalt are shown in Table II. The dynamic mechanical properties of this asphalt have been described in previous publications [17, 18]. The

TABLE I Composition of borosilicate glass (Pyrex^{TM})

	Percent
SiO_2	80.6
B_2O_3	11.9
Al_2O_3	2.0
Na_2O	4.4
Ca or Mg	1.1

TABLE II Properties of Shell Venezualan asphalt

	Temperature, °C		*ASTM Test*
Viscosity, Pa·s	60	1519	D-2170
Penetration	5	10	D-5
	25	96	
Penetration Index		−1.3	
Ductility	4	11.5	D-113
	25	150+	
Flash Point, °C		299	D-92
Density, g/cm^3	25	1.011	D-70

maximum in the tan δ curve for this particular bitumen (Shell Venezualan) is near 0°C with a corresponding glass transition temperature of −25°C. Iron naphthenate (6 percent iron by weight) was obtained from Nuodex Canada Ltd. Iron oxide (Fe_2O_3-red, anhydrous), and calcium oxide were purchased from the Fisher Scientific Co. Naphthenic acids are monocarboxylic acids derived from petroleum [19].

Peel Test Procedure

The adhesion of the asphalt to the glass plate was measured using an Instron Testing machine equipped with a 90° angle peel tester as shown in the diagram (Fig. 2). The 90° angle was maintained throughout the test by a sliding carriage. The cleaning procedure for the borosilicate glass plates followed the method of Zisman [20]. After cleaning in laundry detergent, the glass plates were immersed in aqueous sodium hydroxide (1.0 percent) at 90–95°C for 5 minutes, rinsed, neutralized in hydrochloric acid solution (5 percent) and finally rinsed again with distilled water. The cleaned plates were stored in distilled water until required for testing. The glass plates were oven dried at 110°C for one hour just prior to use.

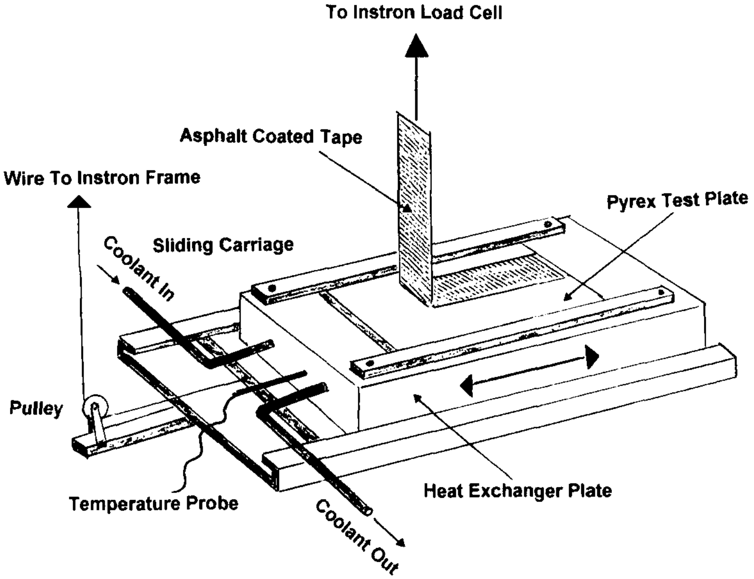

FIGURE 2 The ASTM B533-70 peel test apparatus was adapted for measuring the adhesion of asphalt to various planar substrates. In this experiment borosilicate glass was selected as a model aggregate surface. Glass cloth was used to support the asphalt binder as it was peeled from the glass surface. The sliding carriage is temperature controlled.

After drying, the hot asphalt mixture was carefully poured along the length of the Pyrex glass plate in the middle portion. Metal shims (0.60 mm × 1 cm × 8 cm) were placed on either side of the asphalt strip and a glass cloth (6.5 cm × 23 cm satin weave) was placed onto the molten asphalt. A sheet of paper was placed over the glass cloth and a second glass plate placed on top of the paper. A weight (6 kg) was placed on the assembly for 5 minutes so that the glass plate rested on the shims and provided a predetermined tape thickness. The completed assembly is illustrated in Figure 3. The paper prevents the asphalt from sticking to the upper plate. After removing the upper plate, the completed test specimens were stored at room temperature for about 3 weeks before they were immersed in distilled water.

After various periods of immersion at room temperature, the test specimens were removed from the water and placed in the Instron carriage for peel testing (ASTM B533-70). A utility knife was used to

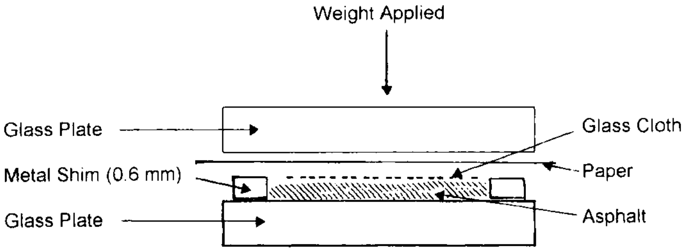

FIGURE 3 Method of preparation of peel test specimens. After heating, the assembly was allowed to equilibrate at room temperature for 3 weeks prior to testing.

cut the middle portion of each sample into a strip 2 cm × 10 cm after which one end could be attached to the Instron grip and pulled at a right angle to the sliding carriage. The temperature of the carriage and test specimens was controlled by a circulating coolant to 15 – 16°C which is near the temperature at which the maximum peel force occurs.

The peel force required to separate the tape from the glass plate was continuously recorded over a length of 10 cm and the average peel force measured from the calibrated Instron recorder chart. The peel rate was maintained at 1.0 cm/min at 15.6°C for most of the experiments. The average value of five independent tests was recorded for each condition.

Chemical Modifications of Asphalt

Portions of asphalt were reacted with maleic anhydride at 100°C for 4 hours to increase the acidity of the asphalt. Other portions were sulfonated with an equimolar mixture of sulfur trioxide and acetic anhydride. The acidified asphalts were then neutralized by hydrated lime. These chemical modification procedures have been previously described by Ciplijauskas *et al.* [21, 22]. The contact angles of the acidified bitumens on glass, before and after neutralization, were determined in both air and water. Since lime is commonly employed as an antistripping agent it was of interest to compare the behaviour of this material in the peel test.

Contact Angle Measurements

The technique described by Neuman and Good [23] was adapted to measure the equilibrium contact angles of bitumen on glass. Small pieces of asphalt about the size of a pin head were placed on a clean dry glass plate and allowed to equilibrate at 100°C in an air oven. After 45 minutes the hot plates were removed from the oven and allowed to cool. After the equilibrated contact angles of the drops had been measured with a goniometer, each plate was immersed in boiling water for 20 minutes, and then allowed to cool to room temperature while remaining immersed. The boiling water softened the asphalt sufficiently so that the droplet could assume a new equilibrium contact angle. The droplet of asphalt reaches its new contact angle equilibrium after 20–30 minutes immersion in boiling water. The plate was removed from the cooled water and the contact angle remeasured. The average contact angles for five independent specimens was recorded. The purpose of these experiments was to determine the effect of moisture on the asphalt/glass contact angle, since the contact angle is considered an indirect measure of adhesion.

The same technique may be applied to any inorganic substrate. Small pieces of aggregate may be polished (to a 1–5 micron surface finish) to produce a flat on one surface. A metallurgical polishing wheel is convenient for this purpose. A small piece of asphalt about 1 mm in size is placed on the flat surface and equilibrated in an oven at 100°C while maintaining the surface in a horizontal position. After removing from the oven and cooling, the contact angle is measured with a goniometer. The specimen is then placed in boiling water in a horizontal position for about 30 minutes to one hour and allowed to cool to room temperature while remaining immersed in the water. When cool, the test sample may be removed from the water and the contact angle remeasured. The change in contact angle after heating in water reflects the loss of adhesion.

RESULTS

The test samples were conditioned at room temperature for about 3 weeks in order to provide sufficient time for the peel force to reach equilibrium. Figure 4 shows that the peel force gradually increased and became constant after two weeks storage. The increased peel force is attributed to minor topographical changes in the asphalt morphology after cooling. The peel force is also sensitive to the thickness of the test specimen. Figure 5 shows the dependence of the peel force on the thickness of the test strip. Metal shims were used to maintain a constant thickness of 0.6 mm for all the peel tests. In general, three distinct types of adhesion behaviour were observed as illustrated in Figure 6. Pure cohesive failures at elevated temperatures produced a relatively constant peel force with minor fluctuations. In the transition region between pure cohesive and adhesive failures the peel force oscillated greatly. This type of failure is referred to as "stick-slip" behaviour. As the adhesion became progressively smaller, the failure produced a clean separation with no visible asphalt residue remaining on the glass surface. The peel force under these conditions is relatively constant and very small. This latter type of behaviour is referred to as "stripping" in the paving industry.

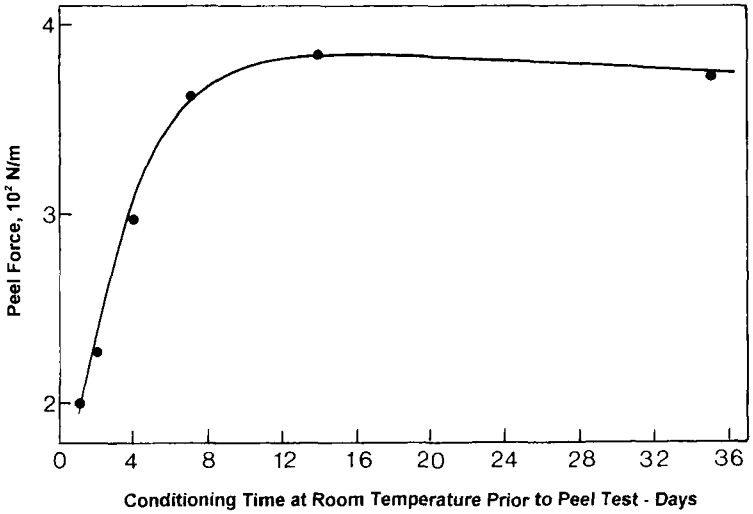

FIGURE 4 After application to the glass plate there is a gradual increase in the peel force of the asphalt binder over a period of two weeks. Therefore, all test specimens were purposely conditioned at room temperature for two weeks until the asphalt had stabilized.

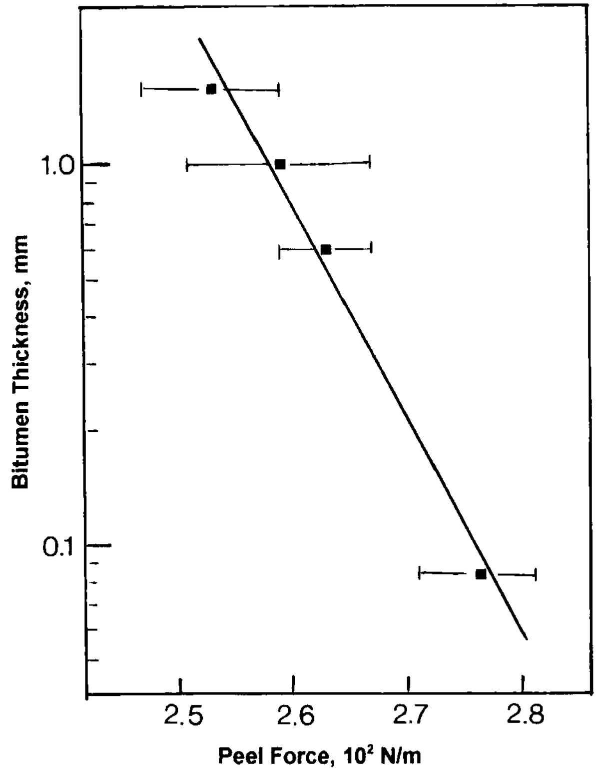

FIGURE 5 The peel force is sensitive to the thickness of the asphalt layer. Therefore, all test specimens were prepared using shims to maintain the asphalt test strip at a constant 0.6 mm thickness. The peel tests were conducted at 25°C.

Temperature has a major influence on the bitumen peel force as shown in Table III. At temperatures above 12.5°C, steady cohesive peeling was observed with minor fluctuations under dry conditions. At lower temperatures, in the region 1.0 – 12.5°C, the mode of failure became increasingly stick-slip with large variations in the minimum and maximum peel forces. Below the freezing temperature of water the peeling became steady and continuous again but a greatly reduced force (100 – 200 N/m). Since the glass transition temperature of Venezualan asphalt is near –25°C, brittle fracture begins to predominate as this temperature is approached. The asphalt chosen for this experiment was chemically modified with one percent maleic

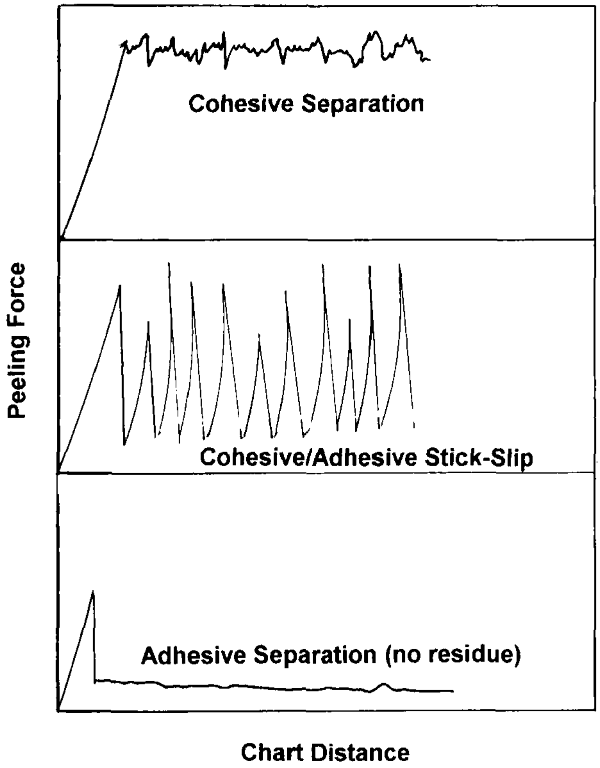

FIGURE 6 Schematic diagram illustrating the three basic types of bond failure in the peel test. The adhesive separation force is about 10 percent of the cohesive strength at the test temperature of 16°C. The stick-slip response is characteristic of mixed cohesive and adhesive failures.

anhydride. The failure mode was cohesive at all temperatures. These tests were carried out under essentially dry conditions.

The severe stick-slip behaviour is attributed to alternating, fast, brittle-type fracture followed by plastic deformation until the stress again reaches a critical value. The increased peel forces at elevated temperatures involve reduced stresses at a blunted crack front attributed to plastic flow. In the absence of moisture the failures are always cohesive.

The peel strength of unmodified asphalt decreased steadily over a period of 24 days while immersed in distilled water, as shown in Figure 7. The failure was initially cohesive in the dry state and was soon

TABLE III Effect of temperature on peel force (dry)

Temperature, °C	*Peel force* (10^2 *N/m*)	*Comments* (*All cohesive failures*)
15.6	11.7	Steady continuous peeling with minor fluctuations.
12.5	9.6	Steady continuous peeling with minor fluctuations.
12.1	0.9 to 34	Mixture of continuous peeling and stick-slip behaviour.
11.4	0.9 to 39	Mainly stick-slip behaviour. Minimum and maximum forces shown.
9.2	0.9 to 30	Stick-slip only.
1.0	1.5 to 20	Stick-slip only.
−5.8	1.8	Steady continuous peeling.
−11.5	1.0	Steady continuous peeling.

transformed to stick-slip behaviour after immersion in water. The asphalt became discolored by the water, turning light brown after prolonged immersion. Complete interfacial failure preceded the formation of the brown discoloration. The peel strength gradually approached zero with complete adhesive failure after 30 days (no visible asphalt residue remaining on the glass plate after peeling). Prolonged immersion of asphalt in water also reduces its cohesive strength. This characteristic behaviour is compared with the same asphalt containing iron naphthenate (0.5–3 percent). After 77 days immersion no significant change in the peel strength was observed and the test was discontinued. The small increase in peel strength over this time span was attributed to physical changes in the asphalt mixture due to water saturation and loss of naphthenic volatiles. It is apparent that a minor concentration of iron has a profound effect on the wet strength adhesion. These observations confirm the findings of Fromm [6]. The optimum concentration of iron naphthenate in asphalt is approximately 0.03 percent iron. It is, therefore, evident that minor concentrations of soluble iron can greatly affect the wet strength retention. Figure 8 shows the effect of various concentrations of the iron naphthenate solution (6 percent iron) on the bitumen peel force after 14–20 days immersion in distilled water at room temperature. The peel force was effectively zero without added iron naphthenate. Significant adhesion retention was attained at a concentration of 0.1 percent iron naphthenate solution since the peeled surface exhibited

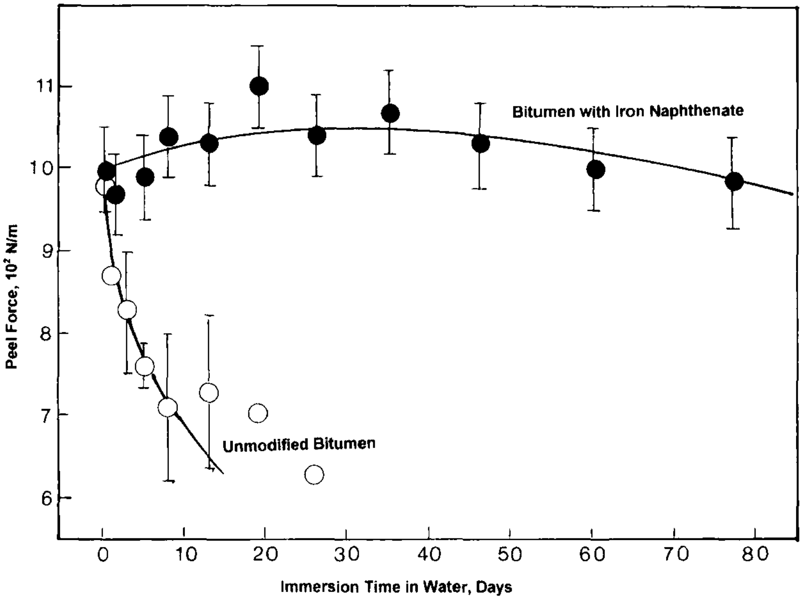

FIGURE 7 The retention of adhesion of asphalt to borosilicate glass while submerged in distilled water is compared with and without added iron naphthenate. Adhesion loss is rapid with unmodified bitumen whereas the same asphalt containing iron naphthenate is virtually unaffected after 77 days immersion.

cohesive separation. The naphthenate solution reduced the viscosity of the bitumen slightly which is reflected in the decreasing peel force as the concentration of the iron naphthenate was increased. A similar trend was apparent for samples aged in air at room temperature. The difference in peel force of 200 N/m between the two curves was attributed to the plasticizing effect of water and solvent on the immersed sample containing iron naphthenate.

Figure 9 shows that ferric oxide is also an effective adhesion promoter, the asphalt retaining full peel strength in water after 17–25 days at concentrations above 1 percent. It is assumed that the iron oxide reacts with the bitumen during the heating period and forms soluble iron species similar to iron naphthenate. Ferric oxide appears to have negligible effect on the viscosity. It is, therefore, significant that the presence or absence of reactive iron species in aggregates can have a marked influence on the wet strength retention of asphalt composites. Both iron naphthenate and iron oxide inhibited the

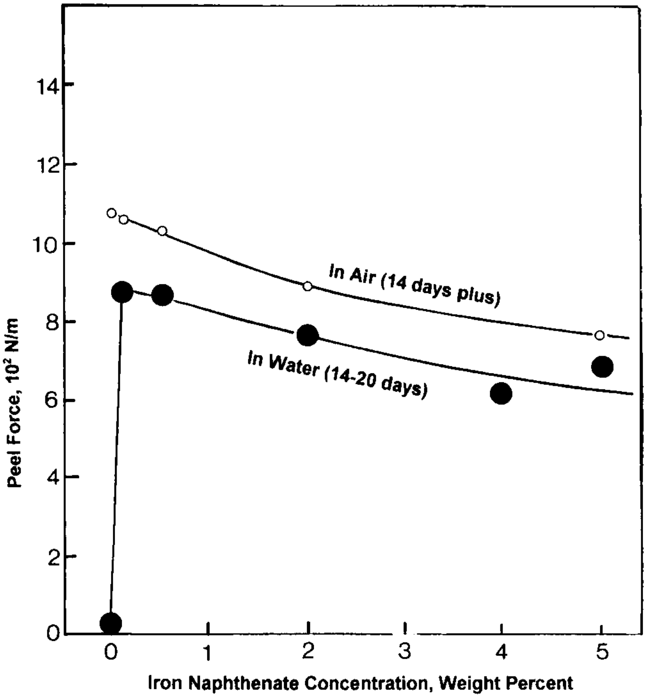

FIGURE 8 The relative adhesion in air and in water is compared for different concentrations of added iron naphthenate. It is evident that iron naphthenate is effective at very small concentrations. The addition of 0.1 percent iron naphthenate is sufficient to maintain cohesive attachment in water. Note that water lowers the cohesive strength of asphalt.

tendency of asphalt to form emulsions with water and become plasticized.

Several attempts were made to modify the surface of glass chemically with iron and chromium as summarized in Table IV. The resulting peel strengths after 20 days immersion in distilled water were significantly improved with all treatments. The combined iron and chromium treatment gave the best results. The increased wet strength adhesion was attributed to bound transition metals on the silicate surface.

Contact Angle Determinations

The surface energy of bitumen is about 33 mJ/m^2 at 25°C [11] whereas the surface energy of a dry silica surface is 560 mJ/m^2 [25]. However,

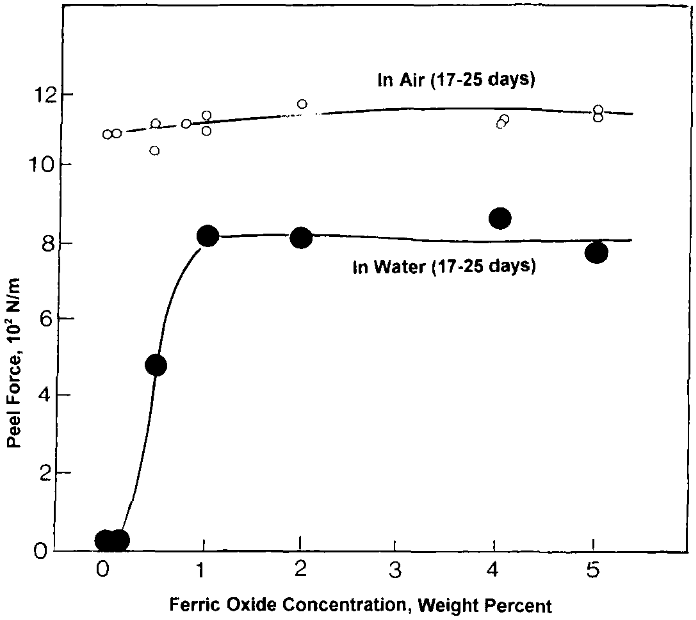

FIGURE 9 Ferric oxide becomes an effective adhesion promoter for asphalt to glass above 1 percent concentration. Full adhesion is retained after 17–25 days immersion in distilled water whereas separation occurs without iron oxide. It is assumed that the iron oxide reacts *in-situ* with heated asphalt to form soluble iron species similar in action to iron naphthenates.

TABLE IV Peel strength of bitumen on borosilicate (Pyrex^{TM}) glass

Surface treatment	*Peel Strength,* 10^2 *N/m*	
	In air after 35 *days*	*In water after* 20 *days*
NaOH/HCl	10.8±1.0	2.5 to 9.2±1.1 (stick-slip)
NaOH/HCl plus FeCl$_3$	10.9±0.1	1.7 to 11.3 (stick-slip)
NaOH/HCl plus ferric acetate	11.0	8.3±0.3 (stick-slip)
Chromic acid	10.8	9.4±1.7
Chromic acid/FeCl$_3$	10.7±1.0	10.6
Chromic acid plus ferric acetate	11.0	8.3±1.2

the surface energy of silica or glass is very sensitive to relative humidity and will approach 22 mJ/m^2 at 100 percent relative humidity due to adsorbed water molecules. The contact angle measurements for a series of samples are summarized in Table V. After heating in an air

TABLE V Contact angles of bitumen on Pyrex glass

Compositions	*In air (degrees)*	*After immersion in boiling water (degrees)*
Bitumen (unmodified)	12.0±0.9	65.6±8.0
Iron Naphthenate		
1/2 percent	10.1±0.9	15.8±1.4
1 percent	11.4±3.0	17.6±4.7
2 percent	10.1±1.1	10.5±1.0
5 percent	12.0±1.6	14.0±1.9
8 percent	9.4±0.9	10.1±1.0
Iron Oxide		
1 percent	11.0	(not determined)
5 percent	16	(not determined)
Maleated bitumen		
1 percent	15.1±2.0	(irregular shape)
5 percent	13.7±2.2	(irregular shape)
Calcium salt of maleated bitumen		
1 percent	24.1±1.6	(irregular shape)
5 percent	19.1±2.1	(irregular shape)
Sulfonated bitumen		
1 percent	20.1±2.0	55.5±11
Calcium salt of sulfonated bitumen		
1 percent	17.9±1.9	69.1±17

oven at 100°C the equilibrium contact angle between Venezualan asphalt and clean Pyrex glass is approximately 12 degrees which indicates favorable wetting characteristics. After reheating in boiling water for 20 minutes the same droplet retracted to an angle of 65.6 degrees, indicating a significant loss of adhesion. When the same experiment was repeated with asphalts containing various concentrations of iron naphthenate, the increase in contact angle after boiling in water was relatively small or negligible. This is further evidence that asphalts containing iron naphthenates maintain adhesion to glass in the presence of water. Since surface energies are relatively independent of temperature, these conclusions are considered valid over a wide temperature range.

The chemically-modified asphalts all showed poor adhesion retention to glass after boiling in water. The introduction of acidic carboxyl groups or their calcium salts onto the asphalt molecule produced unstable droplets and uneven shrinkage in boiling water so that no representative contact angles could be determined after immersion. The contact angles of the sulfonated bitumens showed large increases in the contact angles after water immersion, similar to unmodified bitumen. No immersion trials were conducted with the iron oxide samples.

From the corresponding peel tests it was found that calcium salts accelerated the hydrolysis reaction and the corresponding loss of adhesion. The calcium modified asphalts all showed complete loss of adhesion after 2 weeks immersion in water.

DISCUSSION

In dry situations, the high surface energies of most aggregates will ensure strong adhesion and cohesive type failures with asphalt binders. It is apparent, however, that in a moist environment the formation of a stable interfacial bond is difficult to achieve due to the powerful hydrating effect of water. In the presence of moisture, whether from the atmosphere or from the ground, water molecules will diffuse into the permeable binder and adsorb at the inorganic surfaces to form one or more layers of water molecules. The strong affinity of water molecules for inorganic surfaces will displace any adsorbed organic matter, thereby reducing the work of adhesion to zero. The resulting loss of adhesion can shorten pavement life by causing premature cracking [3].

Since it may require many months for moisture to diffuse into a thick section and reach equilibrium with the surroundings, these destructful tendencies may not become evident for considerable time. Therefore, test methods should preferably be extrapolated to equilibrium conditions in order to predict reliably the long term performance of asphalt pavements. Short term water immersion tests may only influence the surface layers of the test specimens and could provide misleading information about long term durability.

Under laboratory conditions it is possible to prepare clean surfaces without serious contamination with other elements. In practice, most commercial aggregates will contain various concentrations of transition metals such as iron which will affect the water resistance of the composite. The known antistripping behaviour of iron containing aggregates is evidence of the beneficial effect of this element for ensuring long-term water resistance. Given the ubiquitous nature of iron in the earth it seems probable that many aggregates will contain some proportion of this important element. Iron is the fourth largest element in the earth's crust. The evidence in this investigation shows that calcium salts do not promote increased adhesion to clean glass, and may even accelerate adhesive failure. The asphalt binder in this study slowly reacted with water to form a brown-colored paste. This behaviour is apparently characteristic of many asphalts and is attributed to the tendency of asphalts to form emulsified water droplets spontaneously throughout the bulk of the material, converting the binder into a soft brown paste. The presence of lime probably retards or prevents this natural hydration reaction, so that the wet strength as measured by standard procedures (AASHTO T-165 Index of Retained Strength, for example) is significantly larger than it would be without the lime additive. These combined reactions – emulsification with plasticization of the binder and adhesion loss at the aggregate/binder interface – individually and collectively contribute to the destructive effect of water upon asphalt pavements.

The exceptional coupling action of commercial chromium complexes such as Volan™ and Quilon™ have been applied by DuPont for the purpose of promoting adhesion of glass fibres to polyester resins [14]. Since iron and chromium are closely-related elements in the transition metal series, the mechanism of adhesion of these two elements to inorganic substrates is probably similar. It is assumed that the naphthenic radicals are aromatic structures having acidic carboxyl substituents. Similarly, it has been shown that asphalt binders commonly contain acidic functionalities in the form of carboxyl or phenolic substituents [26] which can provide chemical attachments to the iron nucleus as shown in Figure 1. The hexacoordinate structure of the iron atom permits the formation of coordinate bonding with the silicate surface involving 3d orbitals, while at the same time reacting with polar substituents in the asphalt to form hydrolytically-stable attachments.

The situation with calcium oxides is quite different. The calcium oxides or hydroxides are strong bases which will neutralize any acidic components in the asphalt to form insoluble salts. Since calcium salts have different electronic configurations they are unable to form stable coordination complexes. However, basic oxides may help to reduce the water susceptibility of asphalt and retard the emulsification process, i.e., the conversion of asphalt to a brown paste. The published literature indicates that calcium oxide or hydrated lime has a pronounced effect on the modulus of the composite mix [27]. According to Ping and Kennedy [28] the rates of deterioration (as determined by Tensile Strength Ratios) were not significantly different for treated and untreated asphalt concretes subjected to multiple freeze-thaw cycles. No significant difference was found between lime and chemical antistripping additives. Maupin [3] found that stripping is still pervasive in many regions of the United States and difficult to predict from laboratory testing. Stripping was moderate to severe in over 40 percent of the sites examined. Clearly, a more reliable solution to the stripping problem is needed. The presence of water during hot mixing with asphalt should be kept to a minimum, preferably less than 0.7 percent, in order to promote a thorough wetout [29].

Although adhesion and contact angles are related to the respective surface energies, this thermodynamic interpretation excludes other considerations such as voids, penetration, mechanical locking, and oxidative effects. However, adhesion retention under moist conditions is important for durability whether the imposed stresses are caused by weather, thermal cycling, freeze-thaw cycling, or vehicular traffic. The ability of the asphalt binder to resist crack initiation and crack growth is a separate issue [30].

A Quick Test for Wet Adhesion

The reported contact angle measurements relate to the interfacial energy between the bitumen binder and the aggregate surface. The interfacial energy is related to adhesion and is a fundamental material property of the system. The worst-case scenario is obtained when the equilibrium interfacial energy is at 100 percent relative humidity or when the sample is immersed in water. Boiling water liquifies the bitumen so that it is able to flow and readily assume an equilibrium contact angle with the inorganic substrate. A polished surface is mandatory for accurate and reproducible measurements.

The contact angle measurements as described in the Experimental section offer a relatively fast and simple method to determine the wet strength adhesion of an asphalt binder on any particular substrate. Various rock specimens were cut and polished to give a smooth flat surface upon which a small particle of bitumen could be placed for analysis. After equilibrating in boiling water for about one hour the contact angle is remeasured. The extent to which the droplet is able to retain its low contact angle is an indication of its resistance to water stripping. This is illustrated in Figure 10. In general, a contact angle less than 20° will indicate failure in a cohesive manner. Contact angles larger than this are likely to indicate failure in an increasingly adhesive mode with corresponding loss of strength. Thus, an angle of 65° indicates the probability of water stripping. By this method it has been shown that iron oxides and iron naphthenates are effective antistripping agents for mixtures containing sand, limestone or traprock. Since many aggregates may contain traces of iron, the presence of this element could contribute to wet strength retention. The interfacial energy may be calculated from the contact angle using the Young equation [31].

$$\gamma_{sl} = \gamma_{sv} - \gamma_{lv} \cos\theta \tag{4}$$

where γ_{sl} is the solid/liquid interfacial surface energy, γ_{sv} is the solid/vapour surface energy, γ_{lv} is the liquid/vapour surface energy, and θ is the measured contact angle.

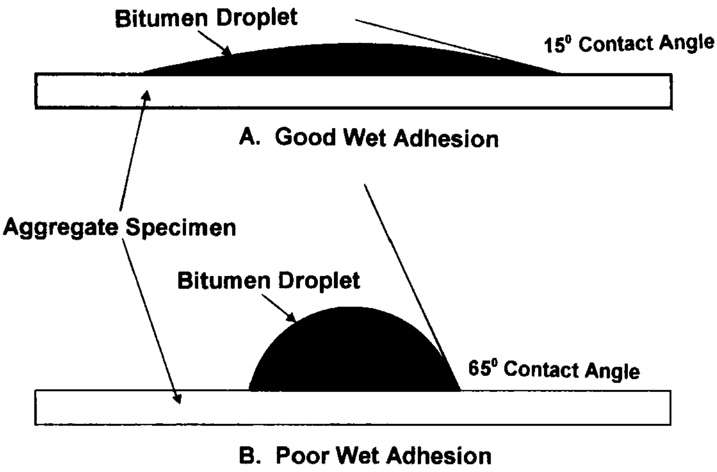

FIGURE 10 In this magnified cross section of a bitumen droplet on an inorganic substrate, the tangent to the bitumen drop subtends an angle which is related to the work of adhesion, W_{adh}. In air the contact angle is about 15°. After heating in boiling water for 30 minutes the droplet will equilibrate to a new contact angle. If the contact angle remains unchanged as in *A*, then the adhesion remains the same. If the drop contracts to a larger contact angle as in *B*, then the adhesion has been significantly reduced. Iron compounds generally confer good wet adhesion in this simple test.

CONCLUSIONS

It has been shown that iron is an important element which can affect the adhesion of asphalt to aggregates when exposed to moisture. Iron complexes, whether added separately or produced *in situ*, function as adhesion promoters in the example of borosilicate glass. Peel tests conducted after 77 days immersion in water revealed no significant loss of adhesion. Contact angle measurements in water corroborated the increased adhesion when iron compounds were present. On the other hand, calcium salts accelerated the loss of adhesion of asphalt to glass during immersion in water. The wet strength retention of asphalt concretes containing lime may be attributed to other factors such as neutralization of the acidic components in asphalt. Although borosilicate glass (Pyrex) was used as a model substrate for silica type aggregates, contact angle measurements indicate that iron complexes can provide increased wet strength adhesion with many other inorganic aggregates including limestone and granite. Iron oxides may also minimize the tendency of asphalts to form emulsions with water by complexing hydrophilic substituents. This reaction may account for the observed increase in modulus and increased tensile strength ratio of these composites.

A simple test is described for evaluating the wet adhesion of asphalt binders to sample aggregates. It is demonstrated that the interfacial contact angle is a fundamental property of the asphalt binder system which governs adhesion. Since the chemistry of each particular aggregate will have an influence on the wet adhesion, it is important to determine the sensitivity of the resulting asphalt bond to moisture. Since iron oxide is both abundant and inexpensive, it may have preventive value as a antistripping additive for asphalt paving materials.

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APPENDIX

The interfacial surface energy of a bitumen/silica interface may be calculated from the Dupre-relationship [A1] wherein the reversible work of adhesion, W_a, between a liquid and a solid per unit area of interface is

$$W_a = \gamma_{sv} + \gamma_{lv} - \gamma_{sl} \tag{A1}$$

where γ_{sv} is the surface energy of the solid surface in equilibrium with the liquid vapour, γ_{lv} is the surface tension of the liquid in equilibrium with its vapour, and γ_{sl} is the interfacial surface energy of the solid/liquid interface. In practise it is important to know if the solid–liquid adhesion remains positive after the system is immersed in water and allowed to equilibrate. After equilibration in water the work of adhesion becomes

$$W_a = \gamma_{sw} + \gamma_{bw} - \gamma_{bs} \tag{A2}$$

where γ_{sw} is the interfacial energy of the solid/water interface, γ_{bw} is the interfacial energy of the bitumen/water interface, and γ_{bs} is the interfacial energy of the bitumen/solid interface. According to Eq. (A2) spontaneous separation will occur if

$$\gamma_{bs} > \gamma_{sw} + \gamma_{bw} \tag{A3}$$

Fowkes [A2] proposed that the interfacial surface energies may be represented by London dispersion forces (γ^d) and polar forces (γ^p) such that the interfacial surface energy between a solid and a liquid may be expressed as

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\sqrt{\gamma_s^d \gamma_l^d} - 2\sqrt{\gamma_s^p \gamma_l^p} \tag{A4}$$

If the individual dispersive and polar components of each substance is known then the interfacial energies may be calculated for each interface in Eqs. (A2) and (A3). Examples of the influence of water upon solid/liquid interfacial surface energies have been published by Van Krevelyn and Hoftyzer [A3]. Table AI lists some published surface tension values for silica, water and bitumen [A4].

Substitution of the values in Table AI into Eq. (A2) yields the following.

$$W_a = 71.5 + 51.3 - 219 = -96.2\,\mathrm{mJ/m^2} \tag{A5}$$

TABLE AI Surface tension components at 20°C (mJ/m²)

	Surface energy	γ^d	γ^p
Water	72.2	22.0	50.2
Silica	287	78	209
Bitumen	33	33	0

The negative work of adhesion implies spontaneous separation of the surfaces. It is apparent that the interfacial energy of a bitumen/inorganic interface will always be larger than the first two terms, so that spontaneous separation is inevitable in the case of physical attractions (dispersive and polar). Therefore, to maintain adhesion in water it is necessary to introduce chemical bonds across the interface which are resistant to hydrolysis.

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