A MODIFIED SHRP NET ADSORPTION TEST

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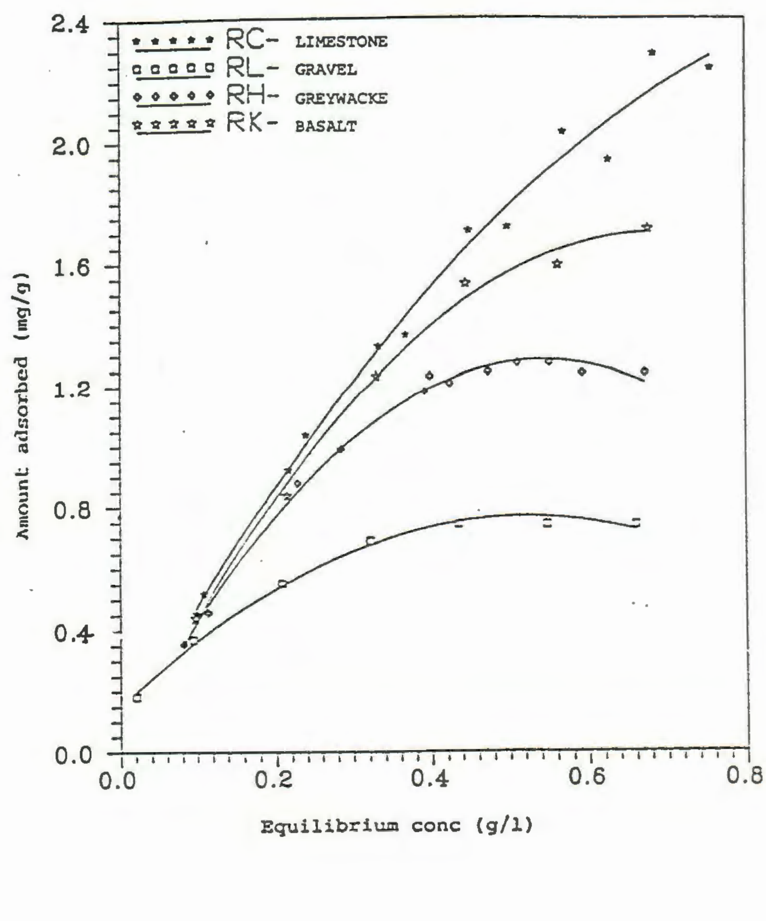
1. INTRODUCTION

The adhesive stability of bituminous materials has been the subject of research since the advent of modern road construction. Studies of the sensitivity of the aggregate-binder bond to water have indicated the strong influence of aggregate type and properties on the bond. Hallberg[2] showed that the adhesion performance of the bond was better with basic (low silica content) than with acidic (silica content >66 percent) rocks.

The Strategic Highway Research Program (SHRP) developed a test for measuring aggregate-binder affinity and resistance to stripping - the Net Adsorption Test[3]. Unlike previous adhesion tests this is based upon measurements of fundamental physical-chemical relationships (adsorption isotherms) between the amount of a solute (bitumen) adsorbed from a solution onto the adsorbent (road aggregate). Adsorption isotherms for four aggregates with one bitumen are shown in Figure 1. The order of greatest affinity of the aggregates for this binder is limestone > basalt > greywacke > gravel. Significant aggregate properties affecting these relationships are the chemical nature and surface area.

FIGURE 1 ADSORPTION ISOTHERMS: ONE BITUMEN WITH FOUR AGGREGATES[4]



2. THE SHRP NET ADSORPTION TEST

The test[3] determines :

(i) The affinity between bitumen and aggregate - Initial adsorption.

(ii) The moisture sensitivity of the aggregate-binder bond - Net adsorption or the amount of bitumen remaining on the aggregate after water is added.

2.1 Procedure (SHRP method M-001)

The test is completed within 24 hours and involves three spectrophotometer measurements of the absorbance (410 nm wavelength) of a bitumen in toluene solution:

(i) initial concentration of the bitumen/toluene solution;

(ii) solution concentration after 6 hours in contact with the aggregate; and,

(iii) solution concentration after the addition of water.

The Net Adsorption is the percent of the initial adsorbed bitumen remaining after addition of water. Performance criteria suggested[5] by SHRP are:

Net Adsorption (percent)	Aggregate-Binder bond performance
> 70	Good
55-70	Marginal
< 55	Poor

3. THE MODIFIED PROCEDURE

In the proposed modified method the aggregate is prepared to the grading shown in Table 1. (SHRP method M-001 requires only that the aggregate should pass the 4.75 mm sieve). As in the case of the aggregate sizes (-40 +80 sieve) used in the SHRP research studies no filler is included. This may be more appropriate since in practice the filler is often obtained from a different source than the coarse and fine aggregates and may contain additives - hydrated lime etc.

With the modified grading the standard deviation on testing an aggregate-binder combinations six times was less than 0.05 mg/g. The standard deviation reported by SHRP was 0.08 mg/g.

All results in this paper are the means of measurements carried out in triplicate.

TABLE 1
AGGREGATE GRADING USED FOR THE MODIFIED TEST PROCEDURE

Sieve Size (mm)	Retained	
	Percent	Weight (g)
2.36	8	4.3
1.18	25	13.5
0.600	17	9.1
0.300	23	12.4
0.150	14	7.5
0.075	6	3.2
TOTAL		50.0

In the SHRP procedure the results are expressed as the percentage net adsorption, which illustrates the susceptibility of the bond to water but does not take into account the amount of bitumen initially adsorbed by the aggregate. This may vary according to the aggregate source: in Table 2 aggregate A has a net adsorption value of 71.3 percent and aggregate B a value of 80.8 percent, which suggests that both are acceptable (i.e. >70). However, if the results are re-evaluated, as suggested by Woodside et al.[1], to express the initial and net adsorption as a percentage of the total bitumen in the solution, a more discriminating assessment of affinity and resistance to stripping is achieved. By this approach it is apparent that aggregate B actually has a lower initial adsorption, 42.7 percent, than A, 48.2 percent and only a marginally better net adsorption value (35.7-35.3).

TABLE 2
RESULTS CALCULATED BY THE SHRP AND THE MODIFIED METHOD

Aggregate	SHRP Parameter A_n (Net)	Modified Parameter[1]	
		A_i (Initial)	A_n (Net)
A	71.3	48.2	35.3
B	80.8	42.7	35.7
Acceptable >70, Marginal 55-70, Poor <55.			

The standard deviation of the modified procedure is 1.7 percent and 1.8 percent for the initial and net adsorption, respectively.

Criteria for acceptable, marginal, and poor initial adhesion and resistance to stripping of mixtures need to be developed for the modified method when sufficient data is gathered.

4. OTHER APPLICATIONS OF THE TEST

4.1 Affinity of Aggregate-Binder Combinations for Surface Dressings

Aggregate-binder adhesion and resistance to moisture damage are particularly important in surface dressings. A review[6] of premature surface dressing maintenance failures in Ireland found that in some cases the properties of the binders and aggregates used may have been a factor.

In this study investigations were carried out to determine if:

(i) the tests carried out on the - 5 mm + 0.075 mm fraction can be used to assess the adhesion and stripping resistance properties of larger aggregate sizes (14 mm to 6 mm); and,

(ii) the test procedure can be adapted to enable bitumen emulsions to be tested (in most countries, emulsions are used predominantly for surface dressing, slurry seals and cold mixes).

4.1.1 Effect of Aggregate Size

Stepwise regression analyses of the SHRP results[4] indicated a strong correlation between certain chemical and physical properties of the aggregate and the results of the net adsorption test. These are summarised in Table 3.

Net adsorption results obtained by the modified procedure are likely to be mainly determined by the chemical composition of the aggregate - variations in surface area would be expected to be minimal and thus have a minimal effect on adsorption because of the use of the standard aggregate grading and the absence of filler.

However, it was uncertain if test results could be used to assess aggregate-binder combinations for surface dressings since there is a disparity between customary sizes used for surface dressing and the aggregate size used in the modified test. It is conceivable that the chemical content of the aggregate surface could change as the size is reduced since crushing and abrasion might occur along planes associated with weaker minerals and thus smaller sizes might have a higher content of weak material, e.g. alumino silicates, than on the surface of larger particles.

TABLE 3

AGGREGATE CHEMICAL AND PHYSICAL PROPERTIES AND NET ADSORPTION[4]

Aggregate Variables	Stepwise Regression Correlation Coeff.
Potassium Oxide Content	0.48
Surface Area	0.71
Calcium Oxide Content	0.75
Zeta Potential	0.87
Sodium Oxide Content	0.90

The aggregates used in this study had a relatively high resistance to polishing (PSV >60), crushing (ACV 19 to 14) and abrasion (<5 to 9). The chemical composition of the surface (mean of measurements on two faces) of 14 mm sized aggregate chippings was determined by an energy dispersion technique (scanning electron microscopy). This was found to be not statistically different from the bulk composition of the crushed aggregate, passing 0.1 mm sieve, (determined by X-Ray fluorescence spectroscopy). These results are shown in Table 4. The difference, between the mean of the two measurements on the 14 mm aggregate particle and the measurement of the bulk composition of the crushed aggregate, varied from less than 1 percent to 5 percent, with the exception of the silica in which case the differences ranged from less than 1 percent to 17 percent, though mostly the difference was less than 10 percent. A t-test comparison for correlated samples showed that these differences are not significant at a level of $p<0.01$.

The authors accepted that, because of the t-test result and as the Na_2O, K_2O and CaO contents are most relevant to the net adsorption (Table 3), measurements conducted using the grading shown in Table 1 can be used as a measure of the affinity and resistance to the effects of moisture for aggregate sizes (normally 10 and 14 mm) used in surface dressing.

4.1.2 Testing with bitumen emulsions

In conducting tests with bitumen emulsion binders the water is removed, prior to testing, by an evaporation procedure. Evaporation of water from a 1 mm film of emulsion is carried out under standard conditions[7]: 55°C in a current of air passing across the binder surface generated by 75 mm water gauge pressure for 18 hours.

Results given by a combination of seven aggregates with emulsions from three sources, shown in Figure 2, indicate that with some aggregates the emulsion source may have a significant effect on the net binder adsorbed. (The source of unmodified bitumens used by SHRP, and also in a limited study of bitumens used in Ireland, had a small effect on the amount of bitumen adsorbed.) Emulsion 1 gave a lower net adsorption than Emulsions 2 and 3 with basalt and granite, and a higher net adsorption than 2 and 3 with gritstone, limestone and Schist B. Emulsion 3 performed best of all with the granite.

The modified test can categorize aggregates in terms of their affinity for a binder. However, if in practice the dust content of a surface dressing aggregate is too high a good net adsorption test result cannot guarantee adequate adhesion and resistance to stripping because the active dust may cause premature breaking of the emulsion before sufficient aggregate coating has taken place.

4.2 Evaluating raw materials for cold mixes

Emulsion bound macadam mixes are being used increasingly[8] in Ireland for roadbases, and stabilisation of wet mix macadams has also been carried out successfully. In Ireland (following French practice) these materials are designed by

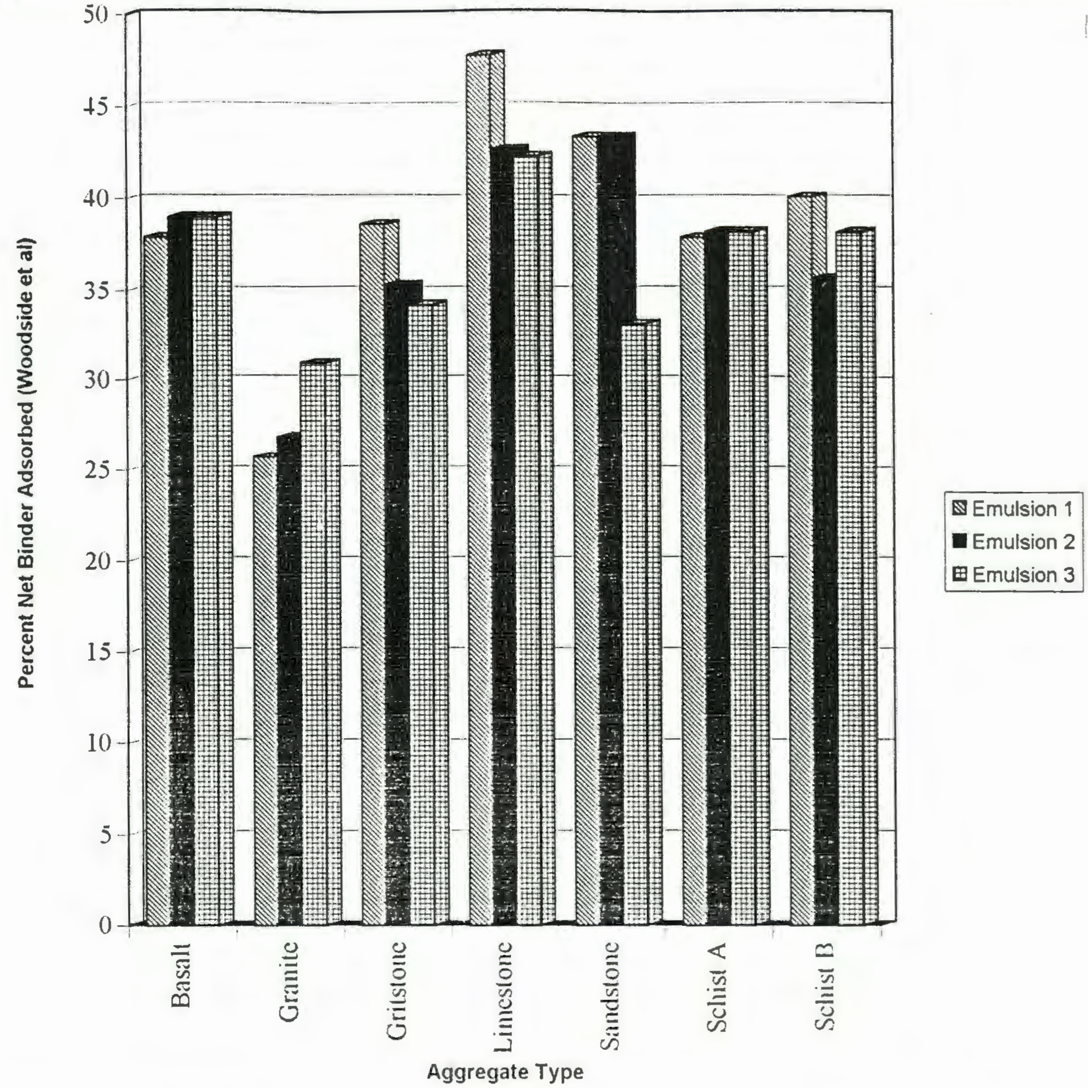
TABLE 4

COMPOSITION OF SURFACE* OF 14 mm AGGREGATE AND BULK AFTER CRUSHING (<0.1 mm)

Element	Basalt		Granite		Gritstone		Limestone		Sandstone		Schist A		Schist B	
	Surf	Bulk	Surf	Bulk	Surf	Bulk	Surf	Bulk	Surf	Bulk	Surf	Bulk	Surf	Bulk
K_2O	1.6	1.7	1.3	0.3	2.7	3.3	2.7	1.1	2.1	1.3	3.7	3.2	4.8	2.5
CaO	4.0	1.5	1.7	0.6	0.7	1.5	32.1	32.5	0.6	0.1	3.2	3.7	3.8	5.1
Na_2O	2.8	4.3	6.4	5.1	2.2	1.0	0.5	0.6	1.1	1.2	1.5	1.3	2.2	1.5
Al_2O_3	18.9	19.2	14.4	12.8	13.5	13.2	9.0	4.2	11.1	7.0	18.0	13.5	21.0	12.4
SiO_2	41.7	51.1	68.2	63.4	65.7	63.0	30.9	30.8	67.7	84.8	52.9	60.2	46.0	57.5
Fe_2O_3	14.0	8.9	5.1	6.1	5.6	5.6	2.9	1.7	3.9	2.7	7.2	5.6	6.3	5.4
MgO	9.5	5.4	1.3	1.3	3.4	2.9	2.7	1.4	1.6	1.0	4.2	3.5	4.9	5.5

* Mean value of one measurement on two faces.

FIGURE 2 MODIFIED NET ADSORPTION TEST: IRISH AGGREGATES AND EMULSIONS



the Duriez dry and wet strength and wet/dry strength ratio. High wet strengths and ratios are taken to be indicative of good resistance to moisture damage. However, the Duriez procedure requires a minimum of 8 days. The ranking of aggregate-emulsion combinations by the more rapid modified net adsorption test might be used as a screening procedure.

Net adsorption test data for the aggregates used in this study are compared with Duriez data in Figure 3. High net adsorption values are associated with low Duriez ratios, and poor behaviour in service. Correlation of Duriez data with performance in service indicates that if the aggregate-emulsion affinity is too high the emulsion breaks before the aggregate has been fully coated. Further investigation of the performance of a wide range of aggregates and emulsions is needed to determine whether the modified method could be used as a rapid screening procedure for selecting aggregate-emulsion combinations for emulsion stabilised bases and subbasess and slurry seals, etc.

4.3 Optimum type and amount of antistripping agents

The use of the Net Adsorption Test for evaluating antistripping agents has been assessed. In these limited studies the aggregate used was a gravel sandstone and the binder was a polymer modified bitumen.

Varying amounts of an antistripping agent (ABA) were added to the binder and these results are shown in Table 5.

FIGURE 3 EMULSION STABILISED MACADAMS: DURIEZ AND MODIFIED NET ADSORPTION

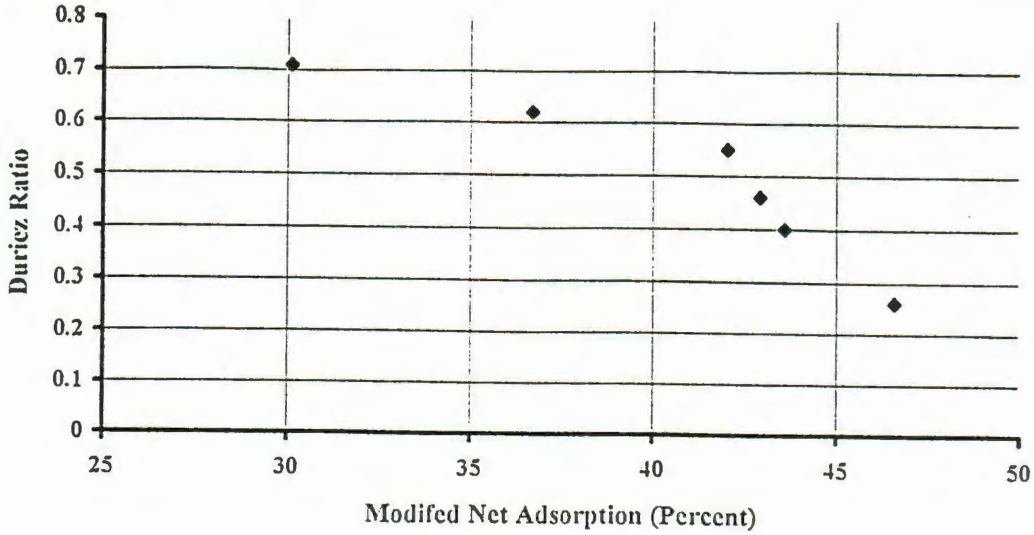


TABLE 5
AMOUNT OF ANTISTRIPPING AGENTS AND NET ADSORPTION TEST VALUES

Binder Type	Modified Adsorption Test (Percent)			Net Calculated by SHRP method (Percent)
	Initial	Net	Desorbed	
PMB	43.2	39.7	3.5	89.4
PMB + 0.3 % ABA	46.8	36.2	10.6	75.2
PMB + 0.6 % ABA	46.4	43.7	2.7	91.3
PMB + 1.0 % ABA	41.2	33.6	7.6	79.3
PMB + 0.5 % ABA	46.4	34.9	11.5	73.4

The initial and net adsorption results (calculated by the modified method) indicate that the optimum effect is achieved with an addition of 0.6 percent of ABA. This was also the optimum when the net adsorption was calculated by the SHRP procedure. The SHRP net adsorption value (91.4 percent), and incidentally the net adsorption value (89.4 percent) obtained without antistripping agent, were well above the SHRP criterion for acceptable performance.

The effect of added surfactants may be unique for the type and amount of surfactant and these results are consistent with SHRP's bond strength measurements(2), Figure 4, which were obtained from sensitive microcalorimeter measurements. The microcalorimeter technique would be too costly and difficult to employ as a routine measuring tool.

5. CONCLUSIONS

1. The modified Net Adsorption test provides a rational quantitative measure of aggregate-binder adhesion and has the potential for ranking alternative combinations of aggregates and binders (including emulsions) for various types of bituminous materials.

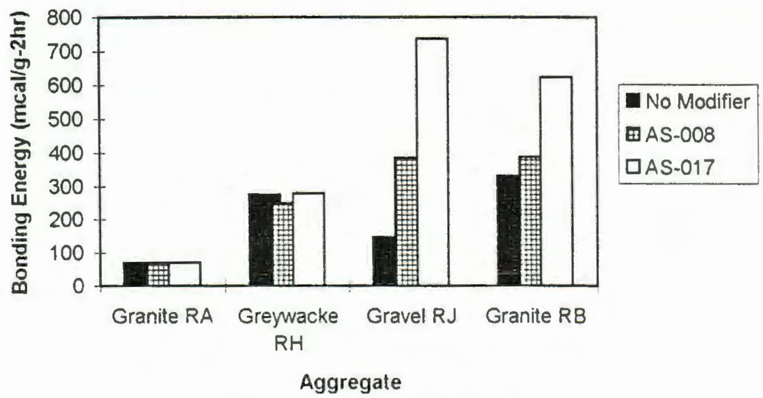
2. The modified calculation procedure gives a discriminating measure of the effects of moisture on the aggregate-binder bond.

3. Further investigation is needed to determine whether the method, which is rapid (1 day) may be used as an alternative or parallel procedure

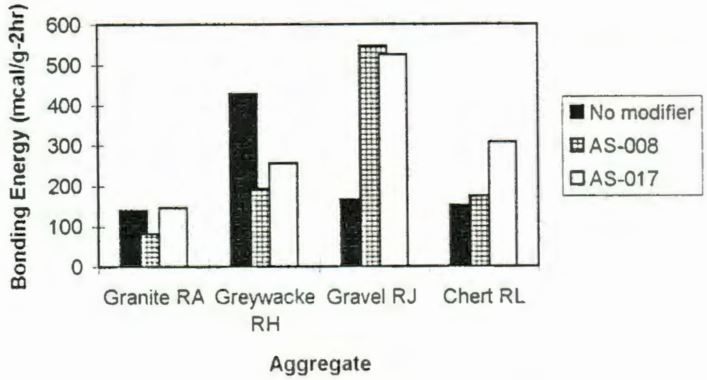
to the lengthy (8 days) Duriez procedure for emulsion stabilised granular materials.

FIGURE 4 SHRP RESULTS: ANTISTRIPPING AGENTS AND BONDING ENERGY

Bitumen AAM +0.05% Modifier



Bitumen AAD + 0.05% Modifier



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