EVALUATION OF A BIOMASS DERIVED OIL FOR USE AS ADDITIVE IN PAVING ASPHALT

J. Houde Jr., I. Clelland, H. Sawatzky, Energy Research Laboratories, CANMET, Natural Resources Canada, 555 Booth St., Ottawa, Ont., Canada, K1A 0G1. E-mail: jean.houde@x400.emr.ca

Keywords: paving asphalt, additive, antistripping

INTRODUCTION

Treatment and disposal costs of sewage sludge can represent up to 50% of a municipality's annual wastewater treatment budget. Sewage sludge (30% solids) accounts 5% of Canadian landfill by weight, and the ever increasing volume of sludge coupled with the decreasing options available for disposal creates a growing problem for major municipalities. Current disposal options are agricultural application, incineration and landfill. Concern about heavy metal migration and public pressure to find a local solution has severely curtailed the spreading of sludge on agricultural land. Incineration is the major option for larger centres but the relatively high cost for incineration, ranging from $350 to $1000/t dry sludge, has caused a great deal of interest in methods of improving the cost effectiveness of incineration or in new equivalent technologies. The high cost and more stringent environmental regulations for incinerating municipal sludges have led to developing more efficient sludge management technologies that are not agricultural based.

The Wastewater Technology Centre of Environment Canada has been developing one such technology since 1982. The thermoconversion process shown in Fig. 1 involves low temperature treatment of sludge to liquid and solid fuel products (1). A key technical feature of the sludge conversion is the formation of a byproduct oil (2) referred to as sludge derived oil (SDO). In 1989, Enersludge Inc., Wastewater Technology Centre and CANMET's Energy Research Laboratories (ERL) of Natural Resources Canada undertook a joint R&D program to be conducted at ERL to investigate promising utilization options for the SDO. SDO is a black, viscous high-boiling (>150°C) organic liquid with a characteristic odour. Initial characterization tests led to investigating the use of SDO as a feedstock material for introduction into a refinery stream. Its average chemical structure is that of a large complex molecule, with a hydrocarbon skeleton and functional groups containing nitrogen (pyrroles, amides) and oxygen (esters). Such structures, which indicate protein origins, tend to be very polar. The relatively high concentration of polar groups in SDO, especially the abundance of nitrogenous groups, and its incompatibility with most distillate hydrocarbons except heavy aromatic gas oils, as discovered in more extensive characterization testing, indicated a more appropriate role as an asphalt additive. This paper describes the work done at ERL to develop SDO for antistripping applications.

COMPATIBILITY

The affinity of SDO for heavy petroleum derived materials was initially investigated by blending equal amounts of SDO in each of ROSE® (residual oil supercritical extraction) residue (3) and CANMET hydrocracking pitch (4). Both were observed to be completely miscible and formed stable viscous blends. The same was then observed with SDO and pentane-precipitated Athabasca bitumen asphaltenes.

Asphalt cement (A/C), a petroleum product made from the fraction that has a boiling point greater than approximately 350°C, contains many polar components including sulphur and nitrogen containing compounds. SDO was found to be compatible with A/C as indicated by the high ductility of SDO and commercial asphalt blends. Incompatibility in an asphalt blend causes a drastic decrease in ductility that is easily detected in comparison to commercial A/C. Ductility is determined by measuring the distance a fixed shape of A/C will stretch at a fixed temperature and rate of elongation until it breaks.

The results of this preliminary investigation as well as the characterization indicated SDO was compatible with A/C. Further, the SDO showed evidence of strong affinity for asphaltenes in asphalt. The high nitrogen content of SDO is desirable for improving of adhesion to aggregate.

ROAD ASPHALTS

Asphaltic concrete road pavement is made from a mix of aggregate (sand, gravel and crushed stone) held together by 5% to 10% on a weight basis of A/C. Government transportation agencies have developed road pavement specifications and are also the largest buyers of road pavement. Their specifications include the hardness of the A/C, its ductility, viscosity, flash point, resistance to stripping and performance after simulated road paving and handling evaluations. Table 1 lists the American Society for Testing and Materials (ASTM) test methods typically used to assess commercial A/C's.

Currently in Canada, A/C is primarily graded on its hardness as measured by penetration, reported as the measured penetration by a needle into a sample of A/C of specified temperature

for controlled time and force (weight) on the needle. Asphalt of 85 dmm (tenths of millimetres) to 100 dmm, i.e., 85/100 penetration, is considered hard, whereas 150/200 penetration is soft.

ANTISTRIPPING ADDITIVE

The resistance to stripping of the A/C from the surface of the aggregate is an important specification for the performance of asphalt pavement and is monitored by the buyers of asphalt pavement. Since A/C does not adhere well to certain aggregates, transportation agencies specify the use of antistripping agents when using these particular aggregates. Stripping involves complex processes which are still not fully understood. Several factors influence the sensitivity of asphalt concrete mix to stripping [5]. For this phenomenon to occur, free water must be present.

Jamieson aggregate (Ontario, Canada) which is prone to stripping and listed by the Ministry of Transport of Ontario (MTO) as requiring at least 1% antistripping agent in the A/C, was chosen to evaluate the antistripping performance of SDO in A/C blends. ASTM test method D-1664[1], the test method for evaluating coating and stripping of bitumen-aggregate mixtures, requires a 95% coverage in static immersion tests to meet specifications.

To demonstrate the stripping resistance of SDO in A/C blends, three commercial A/Cs and various concentrations of SDO were used with Jamieson aggregate as shown in Fig. 2. The results are an average from the visual stripping evaluations of a panel of five evaluators. The coverage of the aggregate by the A/C increased from about 60% (for the first two A/Cs) to above 90% as SDO was added. The retained coverage of the third A/C, with no SDO, increased from about 40% to above 90% as in the above case. Further, the performance of an A/C with one of the commercial antistripping agents, Alkazine-O, recommended by the MTO is shown for comparison (80% retained coating at the 1 wt % level). Under these conditions, SDO has antistripping performance equal to or in excess of that given by at least one commercial agent, and can be used to have coverage in excess of MTO specifications.

Sources of SDO other than the Atlanta SDO (undigested sewage sludge derived oil) were also evaluated for performance as antistripping agents. These samples were also obtained from bench-scale experiments using Highland Creek (Toronto, Canada) sewage sludge, an undigested sludge, and Hamilton sewage sludge, a digested sludge, supplied by the Wastewater Technology Centre. A digested sludge is one that has been subjected to anaerobic bacterial digestion. An SDO from digested sludge has a reduced nitrogen content. In Fig. 3, several concentrations of these two SDOs are compared with commercial antistripping agents: Alkazine-O, Redicote AP and Redicote 82S. Some of these commercial agents are as effective as the SDO at approximately half the concentration. Comparison of Highland Creek SDO and Hamilton SDO (undigested versus digested sludges) as antistripping agents shows a parallel, but slightly less effective performance curve for the digested SDO, indicating the significance of the nitrogen content of SDO as a factor in adhesion to aggregate.

The use of antistripping additive may cause significant modifications to other performance properties of asphalt cement. The other properties of asphalt cement susceptible to modifications were also assessed. Candidate blends of asphalt cement with SDO and commercial antistripping agents were evaluated for asphalt cement performance specifications in Table 2. Blends of 2% Redicote 82S were compared with SDO blends as well as several other commercial antistripping agents. These results indicated the performance of SDO at 5% does modify the asphalt cement test results, in particular the loss of volatiles in the thin film oven test and the penetration. The changes to the penetration of the asphalt cement can be modified by a change in the distillation temperature of the SDO fraction or a change in the consistency of the A/C. However, there may be a limit to the acceptability of a change in penetration caused by an additive unless the A/C is very hard. It should be noted that the use of only 2% SDO with the A/C3 in Fig. 2, was successful for all specifications monitored. Further, the viscosity of the SDO containing asphalt cement easily met the MTO criteria.

In an effort to further define the antistripping performance curve, SDO was again tested by the stripping immersion method including the 3 wt % additive level. The results in Fig. 4 show that the 3 wt % additive level was as effective as the 5 wt % additive level in both 85/100 and 150/200 penetration A/C4. The 3 wt % additive level resulted in less change of the A/C's consistency, as shown in Table 3. In another phase of testing, a one year old SDO sample was compared to a freshly obtained sample. There was no significant difference in effectiveness as an antistripping agent between the SDO samples, indicating the stability of the product.

[1] Summary of ASTM D-1664 : The selected and prepared aggregate is coated with the bitumen at a specified temperature appropriate to the grade of bitumen used. The coated aggregate is immersed in distilled water for 16 to 18 h. At the end of the soaking period, and with the bitumen-aggregate mixture under water, the total area of the aggregate on which the bituminous film is retained is estimated visually as ≥ 95%.

MARSHALL TEST

The next logical step was to test how SDO as an A/C additive compared to a commercial additive in the asphalt concrete. One of the standard testing methods commonly used is known as the Marshall test. The A/C and selected aggregate are mixed hot to produce an asphalt concrete which is compacted by a laboratory compactor, simulating the roller compaction the concrete would receive in the field. The cooled asphalt concrete sample is tested for strength and resistance to plastic flow with an applied lateral force.

A standard HL-3 mix design was used for manufacturing all specimens to be evaluated. The ratio of coarse to fine aggregate was 40/60. Each specimen contained 5% A/C. Specimens were manufactured according to MTO LS-261 and tested according to MTO LS-263 and LS-264 procedures for resistance to plastic flow using Marshall apparatus and theoretical maximum relative density, respectively. Table 4 gives the results for the Marshall stability of 5% SDO and 2% Redicote 82S blended in 85/100 penetration A/C. Three duplicate determinations were done on each sample. The results show that the SDO blend performed as well as the commercial antistripping agent, Redicote 82S. The SDO addition did not lower the Marshall stability of the samples studied.

RECYCLED ASPHALT

When asphalt pavement is exposed to atmospheric conditions for several years, it degrades by becoming harder and more brittle. For this reason, asphalt pavement must be replaced or drastically repaired at the end of its typical age of 12 years. One notable effect of aging on asphalt cement is the increase in the asphaltene content. Attempts at softening aged asphalt cement by adding low viscosity high-boiling petroleum oils were unsuccessful because these oils do not accommodate the increase in asphaltene content. A successful agent for softening or rejuvenating aged asphalt cement must be able to disperse or peptize the asphaltenes. In general, very soft asphalts, referred to as fluxes, are used to rejuvenate aged asphalts because they can absorb the effect of the increased asphaltenes. Given the excellent ability of SDO to dissolve the CANMET residue, the ROSE® residue, and the Athabasca asphaltenes, it was expected that SDO would rejuvenate aged asphalt. Further, the softening and reduction in penetration observed in blends of SDO and virgin asphalt cement are also desirable.

A sample of aged asphalt cement was obtained from a local asphalt pavement replacement operation. Milled asphalt pavement was extracted with toluene and the aged asphalt cement was recovered by evaporation. The aged asphalt cement was blended with SDO. The penetrations and kinematic viscosities are shown in Table 5.

Further, Bow River crude asphalt of 454°C was blended with the aged asphalt. Bow River asphalt is very soft and is considered to be a high quality flux, which is ideal for rejuvenating asphalt. The results indicate that hard, aged asphalt cement of 30 dmm penetration can be softened to make the equivalent of 85/100 penetration grade asphalt cement. Only 12% SDO was required to make this penetration whereas more than 22% Bow River flux is required. However, the viscosity of 22% Bow River flux in asphalt cement is just above the MTO kinematic viscosity minimum of 280 cSt. If more Bow River were added to make the 85/100 penetration grade of asphalt cement, it would probably just fail the viscosity specification.

SDO performance in hot mixed recycling was investigated using the thin film oven test. The results in Table 6 show that 9% SDO passes the TFOT weight loss specification, as well as improves the viscosity of recycled asphalt cement. While the penetration is below the 85/100 specification, it is possible that either a soft flux can be used, or further addition of SDO can be utilized to soften to a penetration of 85 dmm.

One additional benefit of using SDO for rejuvenation is its property as an antistripping agent. A 9% blend of SDO into aged asphalt cement had a static immersion coverage of 100% on Jamieson aggregate. The unmodified, aged asphalt cement had a coverage of only 42%. The results of SDO rejuvenated asphalt cements in the thin film oven test are also encouraging. As shown in Table 6, when 9% SDO was added to an aged asphalt cement and subjected to the thin film oven test, a 60% retention of the penetration occurred along with a weight loss of 0.60%. Both meet the ASTM D-946 specification.

These results show the performance of SDO as a rejuvenating agent. Not only does it perform well for rejuvenation, softening, and asphaltene compatibility, it also improves the stripping resistance of the rejuvenated asphalt cement. This increases its value over other agents to recyclers of asphalt pavement. Further, it should be noted that the amounts of SDO used are reported as a fraction of the aged asphalt cement. While this may represent a small amount on the scale of recycled pavement, methods to contact the aged asphalt cement with SDO must be considered.

CONCLUSIONS

It has been demonstrated by extensive antistripping studies conducted on the different SDO samples supplied to ERL that the SDO antistripping properties are independent of the process used to produce the sludge derived oil (bench scale versus pilot scale), and relatively dependent on the sludge type (digested versus undigested). The digestion process removes some materials that would be converted to SDO in the oil from sludge process. The SDO from digested sludge also is less effective as an antistripping agent relative to the SDO from undigested sludge.

A 3% SDO concentration was found to be as effective as 5% SDO concentration for stripping inhibition. Furthermore, when SDO was used at 3% concentration, the A/C's properties (penetration, viscosity and weight loss after TFOT) were not modified as much as when a 5% concentration was used. If one would like to use 5% SDO, the starting asphalt cement should be in the 60/70 penetration grade to produce a final A/C in the 85/100 penetration range. A comparison of the performance of the year old SDO sample with a fresh sample at the 5% additive level showed no major difference confirming that the SDO is very stable over time and does not lose its beneficial properties.

The addition of SDO can be done either by the wet mode (standard method) in which the additive is blended with the A/C or by the dry mode in which the aggregates are prewetted with SDO before adding the A/C. In the latter case, asphalt engineering/performance tests would be required to confirm that this method does not affect the performance. This is being addressed in road pavement test strips.

The SDO Marshall stability (strength test) was found to be comparable to that of a commercial additive although a greater concentration of SDO is needed. Neither of these additives showed improvement or loss of stability over the commercial virgin asphalt used as control indicating no negative effect on the strength of the asphalt concrete.

Annual demand for antistripping agents for road asphalts in Ontario is valued at approximately $1 million (6). It is estimated that up to 1000 t/a of SDO could be used in such an application. Initial experimentation has also shown that SDO shows promise as a rejuvenant for aged asphalt cement. Not only does SDO perform well for rejuvenation, softening, and asphaltene compatibility, it also improves the stripping resistance of the rejuvenated asphalt cement. This increases its value over other agents to recyclers of asphalt pavement. Recycling asphalt pavement is not a mature technology. Many opportunities exist to advance this technology. As the aggregate resources close to major centres become depleted, this technology will undoubedly receive more attention.

ACKNOWLEDGEMENTS

The authors wish to thank P. Mourot and D. Martinoli of Enersludge Inc. and H. Campbell of WTC for their financial and technical support and their assistance in interpreting the results of this work. The authors also wish to thank J. Odgren of the Regional Municipality of Ottawa-Carleton's Material Testing Laboratory for technical support and interpretation of the Marshall Test portion of the research. Federal support of this work was provided through the Federal Program on Energy Research and Development (PERD).

REFERENCES

1. Campbell, H.W. and Bridle, T.R. "Sludge management by thermal conversion to fuels", Proc. of New Directions and Research in Waste Treatment and Residuals Management, Vancouver, 1985.

2. Campbell, H.W. and Martinoli, D.A. "A status report on Environment Canada's oil from sludge technology", Proc. of Status of Municipal Sludge Management for the 1990s, WPCF Specialty Conference, New Orleans, 1990.

3. Gearhart, J.A. and Nelson, S.R. "Upgrading heavy residuals and heavy oils with ROSE", Energy Processing/Canada, May-July, 1983.

4. Poirier, M.A. and Sawatzky, H. "The utilization of process residues for the production of road asphalt cements", Proc. of 30th Annual Conference of the Canadian Technical Asphalt Association, Moncton, 30, 42-58 (1990).

5. Stolle D.F.E. "Silane coupling agents to reduce moisture susceptibility of asphalt concrete", MTO Report #PAV-90-04, November 1990.

6. Kennepohl, G.J., MTO, personal communication, 1990.

Table 1 - ASTM asphalt cement specification tests

ASTM method	Test description
ASTM D-5	Penetration of bituminous materials
ASTM D-92	Flash Point, Cleveland Open Cup
ASTM D-113	Ductility of bituminous materials
ASTM D-1754	Effect of heat and air on asphaltic materials
ASTM D-2052	Solubility of asphalt materials in trichloroethylene
ASTM D-2170	Kinematic viscosity of asphalts
ASTM D-2171	Viscosity of asphalts by vacuum capillary viscometer

Table 2 - Atlanta SDO in asphalt cement

								THIN FILM OVEN TEST						
Test	Strp. Imm.	Penetration 4°C,25°C,30°C	Flash Point	Viscosity Absolute 60°C	Viscosity Kinematic 135°C	Ductility	TriClEth. Solubility	Weight Loss	Penetration 25°C	Retained Penetration	Viscosity Absolute 60°C	Viscosity Kinematic 135°C	Ductility	Strp. Imm.
Units	(%)	(dmm)	(°C)	(P)	(cSt)	(cm)	(%)	(%)	(dmm)	(%)	(P)	(cSt)	(cm)	(%)
A/C4 85/100														
0% SDO	38	8, 98, 158	324	1573	332.1	+150	99.93	0.02	53	55.2	3178	446.2	+150	25
5% SDO	96	13, 156, 189	248	1044	228.0	+150	99.85	0.91	75	48.1	1756	340.3	+150	94
2% Redicote 62S	74	13, 121, 144	300	1043	278.0	+150	99.93	0.16	68	56.2	1915	387.3	138	97
1% Naldad	94													
A/C4 150/200														
0% SDO	20	15, 174, 216	316	476.1	191.8	130	99.95	0.00	99	56.9	799.5	244.0	-	
5% SDO	95	19, 242, 301	264	315.1	141.6	+150	99.85	0.84	132	54.5	613.5	183.7	+150	95
2% Redicote 62S	85	16, 194, 292	304	389.4	168.8	+150	99.96	0.08	138	71.1	569.0	207.8	+150	95
1% Naldad	87													
1% Alkazine 0	75													
A/C3 85/100														
0% SDO	39	6,83			392.0									
2% SDO	95	9,91	266	1292	327.0			0.30	62	68.1	3532	512.0		
1% Alkazine 0	60													
Spec ASTM D946														
85/100	+95*		>232	>280**		>100	>99	<0.85		>47			>75	
150/200	+95*		>220			>100	>99			>40				

*Spec ASTM D1664
**Spec MTO ls-202

\tab2sdo.wk3

Table 3 - Performance of SDO in asphalt cement

							THIN FILM OVEN TEST					
Test	Penetration 4°C,25°C,30°C	Flash Point	Viscosity Absolute 60°C	Viscosity Kinematic 135°C	Ductility	TriClEth. Solubility	Weight Loss	Penetration 25°C	Retained Penetratio	Viscosity Absolute 60°C	Viscosity Kinematic 135°C	Ductility
Units	(dmm)	(°C)	(P)	(cSt)	(cm)	(%)	(%)	(dmm)	(%)	(P)	(cSt)	(cm)
A/C4 85/100												
0% SDO	7, 82, 135	292	1557	328.8	+150	99.86	0.00	58	71	3574	461.5	+150
3% SDO	11, 104, 204	244	1006	259.4	+150	99.80	0.72	62	60	2456	363.6	+150
5% SDO	11, 126, 238	226	768.4	227.2	135	99.69	1.24	68	54	2236	354.6	+150
0% SDO old	6, 98, 156	324	1573	332.1	+150	99.93	0.02	53	55	3176	446.2	+150
5% SDO old	13, 156, 189	246	1044	226	+150	99.85	0.91	75	48	1756	340.3	+150
A/C4 150/200												
0% SDO	12, 141, 253	296	716.2	237.0	149	99.81	0.01	79	56	1426	316.4	+150
3% SDO	15, 173, 307	266	510.6	192.2	128	99.83	0.80	99	57	1421	282.8	+150
5% SDO	17, 227, 372	232	420.2	166.5	115	99.89	1.24	107	47	977.6	254.4	+150
0% SDO old	15, 174, 218	316	476.1	191.8	130	99.95	0.00	99	57	799.5	244.0	--
5% SDO old	19, 242, 301	264	315.1	141.6	+150	99.85	0.84	132	54	613.5	183.7	+150

Table 4 - Marshall stability tests (MTO LS-263)

	Sample #	Stability (KN)	Flow (.001 in.)	V.M.A.* (%)	Air Voids (%)
Control	I A	11.225	9.50	15.09	6.00
	I B	11.002	9.90	14.88	6.20
	II A	12.622	---	13.57	4.88
	II B	12.958	11.00	13.61	4.96
	IIIA	13.972	10.12	14.33	5.56
	IIIB	12.292	10.72	15.25	6.45
5% SDO	I A	14.330	9.10	14.17	5.47
	I B	11.063	8.20	14.59	5.38
	II A	10.448	---	13.47	5.28
	II B	10.995	9.40	13.29	4.72
	IIIA	12.993	10.76	12.54	4.12
	IIIB	13.612	9.10	13.02	4.14
2% Redicote 82S	I A	6.687	2.80	18.46	2.58
	I B	6.689	3.00	16.35	2.59
	II A	12.017	9.40	14.14	5.83
	II B	10.585	10.50	14.38	6.28
	IIIA	12.545	8.34	14.40	6.34
	IIIB	14.784	9.09	13.83	5.78

* V.M.A. - Voids in mineral aggregates
Calculated by the following formula: V.M.A. = 100 - [C (100-AC)/G]
where C = Bulk specific gravity of compacted bituminous mixture
AC = Wt % asphalt cement (A/C)
G = Maximum specific gravity of aggregate, assumed at 2.70
All mixes made with 5% by weight A/C - 85/100 penetration
Coarse aggregate (>#4 US Sieve) - Jamieson [40 wt %]
Fine aggregate (<#4 US Sieve) - Dibblee [60 wt %]

Table 5 - Comparison of penetration and viscosity in AAC[2] using different additives

	Penetration (dmm)		Kinematic viscosity (cSt)	
	4°C	25°C	100°C	135°C
AAC	7	30	11039	866
AAC + 2.1% SDO	7	40	6883	719
AAC + 6.0% SDO	7	50	4794	624
AAC + 12.2% SDO	11	98	4801	413
AAC + 22.0% Bow River 454°C	13	80	3079	287
Bow River 454°C	>300	n/a[3]	67	21
SDO	>400	n/a	22	7

Table 6 - AAC properties before and after addition of SDO

					Post TFOT		
A/C	SDO (%)	Viscosity @ 60°C (P)	Penetration @ 25°C (dmm)	TFOT wt loss (%)	Viscosity @ 60°C (P)	Penetration @ 25°C (dmm)	Retained pen[4] (%)
AAC	0	29 720	32	0.03	45 210	-	-
AAC	9	5 330	65	0.60	9 583	39	60

[2] AAC: Aged asphalt cement
[3] n/a: not analyzed
[4] Pen: Penetration

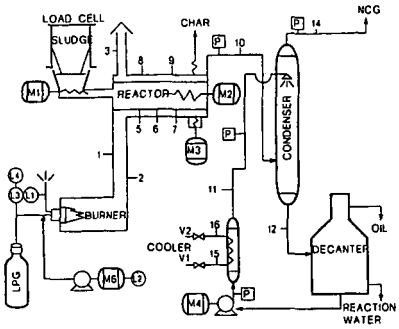

Fig. 1 - SCHEMATIC OF OFS PILOT PLANT, HAMILTON, ONTARIO

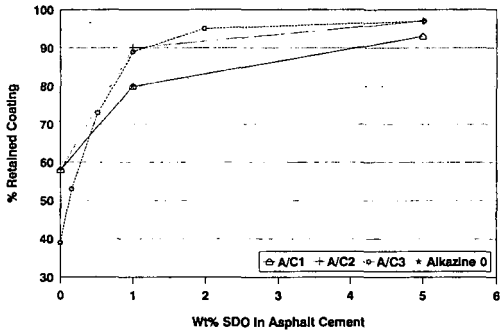

Fig. 2 - STRIPPING BY STATIC IMMERSION TEST

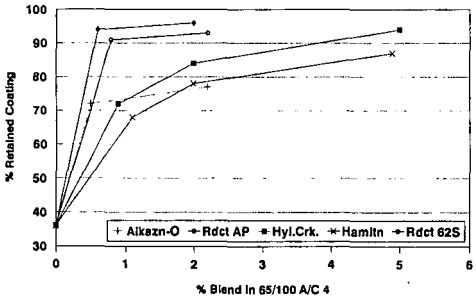

Fig. 3 - ANTISTRIPPING TEST ADDITIVE BLENDS VS RETAINED COATING

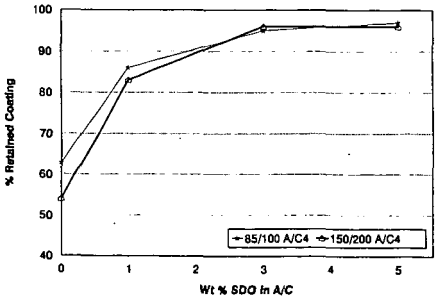

Fig. 4 - STRIPPING BY STATIC IMMERSION TEST