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Flamespray Coating as an Environmentally Acceptable Pavement Marking Technique

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FLAMESPRAY COATING AS AN ENVIRONMENTALLY ACCEPTABLE PAVEMENT MARKING TECHNIQUE

Executive Summary

Powder coatings for flamespray application as pavement markings are not generally available and are not popularly used for the purpose in the US. The relatively high cost of the typical resin powders designed for flame spraying and the fact that the technique has rarely been used in pavement marking probably discouraged its exploration.

In this effort we have attempted to formulate a powder coating suitable for the purpose, using commercially available alkyd type resins presently used in thermoplastic pavement markings. Modifying the coating formulation mainly involved removing the mineral oil plasticizer/lubricant content in the compound and replacing it with a polyamide resin at a level of 5-20 percent. The resulting blend had to be reduced in particle size to allow flamespray application. This could be achieved using cryogenic grinding or the less expensive ambient-temperature grinding of the resin. The resulting product could be flamesprayed onto concrete substrates and showed good adhesion and abrasion resistance.

The main drawbacks of this approach are that the glass beads cannot be mixed into the formulation, but has to be used as a "drop on" application immediately following the resin spraying, and that the available spray guns need to be modified or redesigned to obtain better edge definition. These modifications are in principal quite feasible.

The product being based on thermoplastic type resin has good engineering characteristics as well as good environmental acceptability. Flamespray compounds are essentially no-VOC formulations that are 100 percent solids. The trial formulations developed here to establish feasibility can be further modified to correct any deficiencies or to lower costs after all the key characteristics including long-term weatherability has been experimentally established.

1. Introduction

The USEPA recently regulated the allowable amounts of volatile organic compounds (VOCs) permitted in industrial coating and adhesive formulations. Under these rules the category of pavement-marking materials is permitted a maximum of 150g/l (about 1.25 lbs per gallon) of VOCs in the formulations. Furthermore, discussions are already under way to to further reduce the permitted levels of VOCs in coatings. Future regulations may also impose additional restrictions on the use of hazardous air pollutants (HAPs) in coatings. The use of solvent-based paints, water-based paints, two-part paints (polyesters and epoxy), and tapes that require solvent adhesives for their placement, popularly employed in pavement marking today are drastically affected by these and future regulations. However, this regulatory interest in VOCs and HAPs in

pavement markings is important because of the serious health impacts associated with their release into the environment. The potential exposure of striping crews (and perhaps even motorists) to the VOCs/HAPs in pavement marking formulations is well known to be a serious public health concern. Serious health effects are associated with even low levels of some of the volatile constituents in the marking materials.

Given this regulatory environment it is important to rapidly identify and develop cost-effective alternatives to certain types of traditional pavement marking materials. Evaluation of any future marking materials will involve not only the conventional considerations of engineering performance of the material (such as durability or reflectivity) but also their overall environmental acceptability. . A majority of the commonly used pavement marking materials appears to be inadequate from the standpoint of environmental compatibility. .This criterion refers to characteristics such as the VOC content in the formulation, health impacts of volatile constituents, environmental significance of outgassing from the coating, and safety issues related to application or removal of the marking materials. Only certain types of tape (that do not use any adhesives) satisfy the environmental and safety criteria completely, while extrusion-coated thermoplastic systems also appear to be acceptable in spite of possible minimal release of VOCs. But these are among the more expensive marking materials available and a need exists for a novel inexpensive marking material with outstanding engineering performance and a high degree of environmentally acceptability. Of particular interest will be a system that is cost-effective to be used as a replacement for traffic paints.

The federal highways authorities annually maintains nearly 800,000 miles of the nation's highways. About 80 percent of the markings in recent use on the US highways were found to be based on conventional solvent-borne or water-based traffic paints. A very conservative estimate[1] place the VOC load released to the environment from the centerline markings alone to be over 39 million pounds per year! The following Table 1 based on the report[1] from the study summarizes the estimated VOC load associated with different categories of pavement marking materials used in the US. Also given in the table are TLV (Threshold Limit Value) which are the airborne concentration of a volatile compound to which the workers might be exposed daily without any adverse, based on the best available information.

The attributes of a good pavement marking material suggested by the previous study might be summarized as follows.

Engineering Performance

1. Retention of retroreflectivity
2. Retention of Visibility
3. Durability
4. Ease of Use
5. Storage Stability

[1] Andrady, A.L. "Pavement Marking Materials: Assessing Environment-Friendly Performance." NCHRP Report 392. Transportation Research Board, National Academy Press Washington DC (19970

	6. Lifetime Cost
Environmental Performance	7. Low VOC/HAP 8. Low hazardousness to health 9. Safety

Table 1 The Estimated VOC Loads Associated with the Key Pavement Marking Systems .

	Marking System	Estimated VOC Emission (lbs per mile-year–1997 data)	TLV of the VOC Mixture[a] (mg/cu.m.)
1	Solvent-Borne Paint	66-101	604
2	Water-Borne Paint	6-31	262
3	Epoxy	0.1	400
4	Thermoplastic	0.1	-
5	Tape (Low-VOC primer)	0.8	314

a- The TLV value of a mixture of hazardous air pollutants such as paint is calculated from known weight fractions of the compounds in the mixture and their individual TLV values.

While switching over solvent paints to water-based paints can often reduce the VOC load anywhere from 50-90 percent, the emission of HAPs (e.g. methanol) typically used as a co-solvent in water-based formulations, will remain a significant concern. Some sacrifice in performance and a significant investment in equipment redesign is also usually involved in changing over from solvent to aqueous systems. In this research effort we have explored the possibility of using a 100 percent solid powder system for pavement marking. Such a system has the obvious advantage of little or no VOC and HAP emissions. Therefore, the availability of an inexpensive and high-performance pavement marking system with desirable environmental characteristics will have a major impact on the pavement marking industry and on the health of transportation workers. Serious health effects are associated with even low levels of some of the volatile constituents in the marking materials.

A desirable replacement marking material for traffic paints would have proven engineering performance, zero or near-zero VOC levels, no hazardous components, long enough service lifetimes to be economically feasible, and will have negligible safety concerns. Among the conventional systems only certain types of preformed tape and thermoplastics appear to come close to these requirements. For instance, a preformed vinyl reflective tape (with no adhesive being used) embedded into place on a freshly-made asphalt pavement perhaps meets to these requirements but is a relatively expensive pavement marking option even after taking into account its long service life. Thermoplastics, are somewhat more economical than tape, and also appears to be environmentally friendly by these criteria. However, the application of thermoplastic markings is somewhat more complicated than that of typical traffic paint. The thermoplastic resins

pre-compounded in the factory and available as a slab has to be melted in the field and extruded as a uniform ribbon on to the pavement using specialized equipment.

The research findings from this effort impact several areas of the transportation industry. Clearly the main impact is in the pavement maintenance area. Restriping the markings on existing highways is a routine maintenance task. The technology proposed here will likely extend the service life of the pavements and strive to reduce the cost of such maintenance. Also, it helps the maintenance engineers comply with VOC regulations now in force. Highway worker safety, particularly the reduction of the potential for inhalation of toxic materials, is a high priority in the pavement delineation industry The proposed technology addresses this need by providing a cleaner marking technology that also helps to conserve the urban environment.

1.1 Research Approach.

The approach used in this effort was to attempt flamespray coating of appropriate resins onto asphalt (and/or concrete) pavements as a cost-effective and environmentally-compatible means of marking. The technique of flamespray coating with powder resin materials has been extensively used in other applications such as bridge maintenance, but has never been adequately tested for pavement marking. We propose to demonstrate the feasibility of using novel powder resins, specially those based on the already established thermoplastic materials, as flamesprayed coatings as an effective environmentally-acceptable pavement marking system. A key study[2] on pavement markings that included flamesprayed thermoplastics was carried out by CALTRANS in 1982. The particular flame-sprayed coating evaluated was based on a specific type of a nylon resin (Versamid, Henkel Corpn.) that is no longer manufactured. Only crosswalks and legends were evaluated as equipment was not available for laneline application. In terms of both delineation effectiveness and durability the flamesprayed Versamid resin matched that of solvent-borne paint (but was lower than sprayed thermoplastic). However, given the melt and spray characteristics of the Versamid resin, it was sprayed on at a thickness of 8 mils, the maximum thickness allowed by the combination of the particular resin and flamespray equipment available at the time. Depositing thicker layers was not possible due to some burning of the resin in the flame and adhesion-related problems. A key objective of the present exercise was to use the modern flamespray equipment to achieve thicker (closer to 20 mil) markings using cost-effective resin types for the purpose.

It is instructive to consider how the set of characteristics expected of a good pavement marking material might be influenced by the use of flamespray technique for its application on to pavements.

Retention of retroreflectivity and to some extent the visibility of a marking is a function of both the

[2] CALTRANS. "Establishing Evaluation of Pavement Delineation Alternatives to Solvent-Based Paints", California Department of Transportation. April 1982.

optical characteristics of the resin as well as the adhesion/embedding of glass bead to the polymer layer. As a very wide variety of resins can potentially be flamesprayed and their formulations can generally be designed to match engineering properties of competing marking materials. While the available flamespray equipment may impose some limitations on "sprayability" of a powder composition that contain glass beads, flamespray technique should be compatible with the "drop on" addition of the beads on to the marking surface. (note that glass beads were not post-applied to the coatings evaluated in the Caltrans 1982 study on flamesprayed markings[2]. This could have contributed towards the lower wet-night retroreflectivity performance.)

2.The lifetime cost of pavement marking is a particularly important consideration in developing an alternative marking system. Overall cost of switching from conventional marking (such as painting) to flamespraying invariably includes capital costs associated with the equipment, the cost of the marking (material and labor) itself, and also depends on the service life of the marking. It is reasonable to expect of the flamesprayed stripes (of equal thickness) to enjoy at least the same 4-6 year lifetime attributed to embedded tape or extruded thermoplastic materials. The cost of labor in flamespray application might be somewhat lower than that associated with conventional thermoplastics application because of the relatively simple equipment. The capital costs associated with the acquisition of flamespray marking equipment is also expected to be low for the same reason, and should not be higher than that of converting equipment traffic painting equipment to handle water-based paints.

The fine, often cryogenically ground, speciality polymer powder generally used in flamespraying of steel is relatively expensive compared to blocks of thermoplastics used in highway marking. However, the powder resins intended for pavement marking on uneven asphalt and concrete surfaces need not necessarily have the same high degree of uniformity in particle size or the fineness generally demanded of resins intended for metal applications. A coarser grade of resin powder that may not require cryogenic grinding and could hence be less expensive is likely to be equally effective. Furthermore, a substantial amount of fillers and pigments might be incorporated into the formulation to reduce cost.

The environmental aspects of thermoplastic resins applied using flamespray technique were already discussed in the introduction. The system also has particular advantages in terms of safety. Maintaining a resin as a powder that is only melted immediately prior to being sprayed on the pavement (as opposed to a dangerously hot liquid melt as in conventional thermoplastic application) makes flamespray application a relatively safe technique. Exposure to a typical flamespray gun at a distance as short as 24 inches does not usually result in worker injury.

1.2 Flamespray Technique

The principal of flamespraying is to melt a plastic material feedstock in the form of a finely divided powder, to accelerate the melt droplets to impact on the surface of the substrate of

interest where rapid solidification and deposit build-up takes place. The melting is achieved during the passage of polymer particles through a flame whose temperature is controlled to allow melting at low residence times. The flame also helps to propel the molten droplets towards the surface, where they coalesce and build-up to yield a thick plastic film. Typically, the compressed air is used along with a fuel gas, usually acetylene, propene, propane or hydrogen, in the flame. Temperatures of up to 3000°C can be achieved in these flame but very high temperatures are undesirable in flamespraying as it can discolor the resin through thermal degradation, or even partially burn the resin. While the upper flame temperature is controlled by these concerns the lower temperature in the flame is limited by the melting characteristics of the polymer. The major limitation of flamespray application is that it is unable to yield uniform thin films (in the thickness range of microns); this limitation is of little consequence in the pavement marking applications where thick films are used. Polymer coatings as thin as 0.05 mm can be achieved on most surfaces using conventional flamespray equipment.

Other than surface cleaning, no pretreatment of the pavement surface is generally expected in flamespray coating. Also, the coatings of molten plastics cool and solidify quickly allowing "no-cone" application of the markings under most weather conditions, with minimal disruption of traffic.

For the technology to be practically relevant, however, the availability of a low-cost thermoplastic material that can be sprayed using the existing equipment or slightly modified flamespray equipment is critical. While a range of thermoplastic powder materials with excellent coating performance has been developed, mainly for flamespray coating of metal structures, these are all generally too expensive to be considered for routine pavement marking applications. A primary focus of the present exercise was therefore to develop a cost-effective resin system that can be used for this application.

2. Results and Discussion.

1.1 Evaluation of cryogenically-ground commercial marking material.

A particularly cost-effective approach to developing a powder coating formulation for flamespray application to pavements would be to base it on the existing thermoplastic materials. The feasibility of the concept was studied using a commercially available alkyd thermoplastic coating. Preliminary investigation of a resin mix from a commercial supplier suggested their basic resin characteristics would be suitable for flamespray application. The exact composition of the commercial formulation we used is proprietary, but a typical thermoplastic pavement marking composition is as follows.

Resin material	16%
Mixed olefins	3%

Plasticizer	2%
Titanium Dioxide*	10%
Calcium Carbonate	49%
Glass beads	30%

*Up to 10 percent by weight of an organic colorant may be used in the case of yellow marking compositions.

The commercial resin sample showed some drawbacks. a) the compound had pre-mixed glass beads and was therefore not suited for the flamespray evaluation; and b) the particle size of the material (even without the glass beads) was too large for uniform flamespraying. We were able to get the manufacture of the thermoplastic compound to custom blend for us samples of the resin with no added glass beads. The particle size reduction was achieved by cryogenic grinding of the material; this is a common approach used in the preparation of powder resins intended for flamespray application. The alkyd resin itself was brittle and the cryogenic grinding converted it into a very fine powder (approximately 70 mesh).

The powder was initially evaluated for flamespray application using an "Innotech 124" advanced flamespray coating equipment. A schematic diagram of the coating equipment is shown in figure 1 and consists of a fluidized bed powder delivery system and a flamespray gun. The latter operates on propane gas (13-20 psi) and compressed air (90-120 psi), and is connected to the fluidized bed of powder coating by a powder hose. The unit consumes about 7 CFM of air (@ 100 psi) and 1.5 lbs/hour of propane during typical operation.The standard version of the equipment used in the present experiments had a powder capacity of 10 lbs (in the canister) and an application rate of 20-40 square feet per hour using standard flamespray resins (not the thermoplastic-based resins developed here).

Results from this initial trial were unsatisfactory mainly because the excessive brittleness of marking material broke it down into very fine particles during the cryogenic grinding. The particle size was too fine for flamespray application and even allowed some separation of the inorganic pigment (chalk and titania) content from the resin particles within the powder bed. As might be expected, this heterogeneity in the powder feed led to very poor flamespray characteristics. The films obtained were of unacceptable quality and were not suited for further testing.

Further investigation of the commercial thermoplastic resin and discussions with the manufacturer suggested the formulation to contain a large amount of a plasticizer or lubricant (a mineral or vegetable oil). While this additive was apparently needed for ease of processing in conventional thermoplastic equipment, it was suspected as being responsible for the poor grinding characteristics of the resin compound. A possible solution was to modify the formulation with a suitable polymeric plasticizer. The large scale processing operation did not allow changing of the plasticizer lubricant, and a new thermoplastic formulation therefore had to be compounded in the laboratory for further investigation.

1.2 Evaluation of a test formulation incorporating a polymeric plasticizer.

The efficacy of a polymeric plasticizer for adequate processing properties and in yielding a particle size (on cryogenic grounding) well suited for flame spraying, was tested by preparing a test formulation of a commercially-available alkyd resin. The base resin selected was a maleated rosin polymer (alkyd type) [CAS 68038-41-5] manufactured and marketed by Arizona Chemicals Inc. under the trade name Silvacoat 7021. The polymeric plasticizer was selected from a range of commercially available polyamides. Polyamides belend easily with most alkyds and are expected to provide a moderate degree of plasticization to the system. The selection from the range of polyamide thermoplastics (trade name Uni-rez, available through Arizona Chemicals Inc.) considered is listed inTable 2. A Uni-rez resin that is low cost and has the high elongation and low enough softening temperature (compared to base resin) best suited for the application was identified from 1 as Uni-rez 2623..

In this experiment 10 and 20 percent by weight of the Uni-rez polyamide was mixed with the base Silvacoat resin. The materials were compounded on a 21mm 36/1 L/D Theysohn co-rotating twin screw extruder running at 235 rpm. The melt temperature was held at 363°F

Table 2: Uni-Rez® Thermoplastic Polyamide Resins Characteristics

Thermoplastic Polyamide Resins	Softening Point, °C R&B	Viscosity Cpt/mpa-5 ® 190 °C	Typical Color Gardener ,40% irt Propanol	Tensile Strength Psi (Mpa)	Elongation, %	Modulus Psi (Mpa)
2610 Series						
Uni-Rez* 2611	132	4000	6	700 (4.8)	550	24000 (166)
Uni-Rez* 2614	127	1400	5	280 (1.9)	100	8000 (54)
Uni-Rez* 2616	130	9000	4	950 (6.6)	650	22000 (152)
2620 Series						
Uni-Rez* 2620	105	2900@160° C	6	1000 (6.9)	50	30000 (206)
Uni-Rez 2623	136	6500	6	1000 (6.9)	400	27000 (186)
Uni-Rez* 2624	162	8000	6	1200 (8.3)	400	26000 (179)
Uni-Rez* 2625	143	1100@180° C	6	350 (2.4)	200	9000 (62)
Uni-Rez* 2626	176	2750@205° C	6	1600 (11)	350	34000 (235)
Uni-Rez* 2628	168	900	6	500 (3.4)	100	12000 (83)
2630						
Uni-Rez*2632	125	2500	6	200 (1.4)	300	5000 (34)
Uni-Rez* 2635	140	4300	5	280 (1.9)	200	3000 (21)
Uni-Rez* 2636	132	6250	5	300 (2.1)	650	4000 (28)
Ini-Rez* 2638	142	4500	5	200 (1.4)	200	5000 (34)
Uni-Rez* 2639*	160	6000	6	400 (2.8)	200	4500 (31)
2640						
Uni-Rez* 2640	162	1500	1	700 (4.8)	75	7000 (48)
Uni-Rez* 2641	144	8500	4	520 (3.6)	700	7000 (48)

Uni-Rez* 2643	125	2100	5	400 (2.8)	250	8000 (55)
Uni-Rez* 2645	138	9000	5	800 (5.5)	800	8000 (55)
Uni-Rez* 2646	121	3000	6	600 (4.1)	350	14000 (97)
Uni-Rez* 2647	137	5500	5	350 (2.4)	350	5200 (36)
Uni-Rez* 2648	145	4500	5	300 (2.1)	150	4000 (28)
Uni-Rez* 2649*	160	7500	5	800 (5.5)	400	13000 (90)
2650						
Uni-Rez* 2651	100	7000	5	380 (2.6)	550	9500 (65)
Uni-Rez* 2653	100	10500	5	450 (3.1)	900	10500 (72)
Uni-Rez* 2656	125	11000	5	550 (3.8)	900	10000 (69)
Uni-Rez* 2659	125	9500	5	400 (2.8)	850	10000 (69)
2660						
Uni-Rez* 2662	100	10000	5	1200 (8.3)	500	24000 (166)
Uni-Rez* 2664	170	205	5	1250 (8.6)	20	40000 (275)
Uni-Rez* 2665	165	11000	5	2000 (13.8)	500	50000 (345)

*** Batch only**

throughout the runs. All material was fed through the rear feed throat, and the extrudate was collected in a water-bath and pellatized downstream. The pellets were light yellow in color and were clear showing little or no degradation during processing. The pellatized compounds were cryogenically ground to obtain a particle size of approximately 60-70 mesh. The powdered resin was stored in airtight containers and evaluated by capillary rheometry and in a trial flamespray test on metal and concrete slab substrate. The capillary rheometry was used to establish that using higher levels of the polyamide plasticizer (from 10 percent to 20 percent by weight) in the base resin did indeed result in a readily observable reduction in the melt viscosity of the resin material. This would be needed not only to facilitate processing of the material but also to make sure that the resin coating layer is not unduly brittle and is able to respond to the thermal expansion and contraction of the pavement.

The flamespraying test, however, could not provide much information as the composition was clear (i.e. was a resin blend without the fillers) and the sprayed on coating was not easily discernible by the naked eye. When sprayed on metal, however, the coating appeared to be uniform and strong. However, the flame spraying of unfilled compound was difficult and a tendency for the softened resin particles to accumulate on the nozzle of the gun causing frequent clogging was observed. In any event a valid evaluation of the flame spray applicability of the material requires the investigation of a complete formulation including the fillers and titania pigment as well.

1.3 Capillary Rheometry on the polymer mixtures.

The capillary rheometry of the blends was carried out on a Kayeness Glaxy V Capillary Rheometer (model 8502). The samples were typically dried under vacuum at 100°C for at least 2 hours. Testing was carried out generally in accordance with ASTM D3835 Standard (Test method for determination of properties of polymeric materials by means of a capillary rheometer. The testing was at a temperature of 170 °C using a Z39 die with a diameter of 1.00 mm and a L/D ratio of 20.. A melt time of 10 sec. And an entrance angle of 130° was used in the test.

The data summarized in the table 3 below shows the shear dependant viscosity at 170°C and a packing force of 200N.

The functional form of the melt viscosity is

$$\text{Ln}(\text{h (Pa-s)}) = a_1 + a_2\{\text{Ln (shear rate (s}^{-1}))\} + a_3\{\text{Ln (shear rate (s}^{-1}))\}^2$$

Table 3. Summary of Viscosity Data for the Blend Samples A and B*.

Shear Rate (s^{-1})	Shear Stress (Pa)	Shear Stress (Pa)	h (Pa-s) –A	h (Pa-s) B
145.9	1221	1047	8.4	7.2
231.1	1745	1570	7.6	6.8
352.7	2617	2617	7.4	7.4
355.1	4013	3664	7.5	6.8
814.8	6107	5758	7.5	7.1
1252.6	9248	8725	7.4	7.0
1921.5	13610	12912	7.1	6.7
2943.0	19892	17798	6.8	6.0
4499.7	27570	23905	6.1	5.3

A = Sample with 90 percent Silvacoat resin and 10 percent polyamide plasticizer.

B = Sample with 80 percent Silvacoat resin and 20 percent polyamide plasticizer.

Coefficients from fitting the data to the empirical equation was as follows.

Blend	a_1	a_2	a_3
10 Percent	1.81	0.12	-0.014
20 Percent	0.26	0.57	-0.05

The values of the coefficients (as well as other data in the table) show the higher level of the polyamide to result in a lower melt viscosity and therefore increases the ease of processing the powdered plastic material. Having a lower melt viscosity is also important in flamespray application of plastics as the molten droplets need to coalesce well into a continuous film at or near melt temperatures.

Based on the rheological data as well as on the basis of the exploratory flamespray evaluation of the material the use of polymeric plasticizer was identified to be a promising approach. The flamesprayed coating of both compositions were of acceptable quality although the on with higher levels of the polyamide was of better appearance. However, while the resin could successfully be cryogenically ground, it still yielded a significant fraction of fines that is not useful in powders intended for flamespray application. Often this problem can be addressed by switching from cryogenic to ambient temperature grinding of the material.

1.4 Compounding of test formulations based on polymeric plasticizer.

Based on the encouraging results from preliminary experiment described above, an effort was made to determine the level of the Unirez polyamide resin required in the blend to deliver the desirable flamespray characteristics as well as durability. This was achieved by compounding a range of thermoplastic powders for testing. However, unlike in the preliminary experiment, the formulations now included an inert filler, calcium carbonate, as well as rutile titania pigment typically used in white thermoplastic pavement marking compositions. The compounds were therefore very close in composition to common thermoplastic pavement marking material except in two respects; the polymeric plastiziser was used in place of liquid lubricants or plasticizers, and no glass beads were used in any of the compounds. The Table 4 below indicates the composition of the different compounds that were prepared. As shown in the table, blends in the range of 4 to 20 percent by weight of the polyamide plasticizer resin were studied. A second variable studied was the weight fraction of the inert filler, calcium carbonate in the compound in the range of 20 to 50 percent. The conditions under which compounding was carried out was already described elsewhere in the report.

Table 4 Composition of the different formulations of alkyd thermoplastic material.

	Alkyd Resin Sylvacote 7021	Polyamide UNI-REZ 2623	Rutile TiO2	Calcium Carbonate	Actual Mix

Mix	%	lbs.	%	lbs.	%	lbs.	%	lbs.	lbs.
1	36%		4%		10%		50%		
		5.40		0.60		1.50		7.50	15.00
2	32%		8%		10%		50%		
		4.80		1.20		1.50		7.50	15.00
3*	28%		12%		10%		50%		
		4.20		1.80		1.50		7.50	15.00
4	20%		20%		10%		50%		
		3.00		3.00		1.50		7.50	15.00
5*	42%		18%		10%		30%		
		6.30		2.70		1.50		4.50	15.00
6*	35%		15%		10%		40%		
		5.25		2.25		1.50		6.00	15.00
7*	49%		21%		10%		20%		
		7.35		3.15		1.50		3.00	15.00

The seven different compounds prepared were reduced to the correct particle size by ambient temperature grinding (as opposed to cryogenic grinding resorted to in the preliminary experiments). Ambient temperature grinding is both economical and less likely to produce a large fraction of fines, compaerd to cryogenic grinding. Approximately 10 pounds of each compound was ground to obtain the test samples. The particles (approximately 60 mesh in size) were sieved to remove any large particles.

1.5 Evaluation of the test compounds.

Two types of evaluations were carried out on the set of seven compounds prepared; a) flamespray application on to concrete to assess the sprayability of the powders; and b) a test for durability based on abrasive resistance of the compositions. Both tests were performed on all samples.

a) Flamespray Evaluation.

The flamespray application was carried out using professional grade flamespray equipment, using a gravity-fed spray gun. This type of spray gun was preferred over the newer designs that are fed from a fluidized bed of the resin powder, to minimize any separation of particles by density during suspension in the bed. Concrete tiles approximately 2" by 1" in dimension were obtained from a commercial supply house and used without any pretreatment. Each composition was loaded on to the equipment and flamesprayed on the concrete slab as a stripes approximately 4 inches in width. As the spray rate was not optimized for the test composition in each case, it often required several passes over the line to get an approximate coating thickness of 15-20 mil (the measurement of the thickness of coating obtained was impractical because of uneven surface of the concrete slab material).

All seven compositions were flamesprayable onto the concrete substrate. However, the compounds #5,#6 and #7 were found to be relatively easier to flamespray compared to others.

This was attributed to the higher weight fraction of resin in these compounds. In general, a higher resin content would yield more molten polymer that is able to bind the inorganic materials relatively more effectively on the surface of the substrate. This would be interpreted as "easy to spray" by a flamespray operator. Neither the "sprayability" nor the quality of the flame-spray applied coating on the uneven concrete surface, could not be quantified in any meaningful manner. The general qualitative observation was that all compounds were flamesprayable with higher resin content being easier to apply using flamespray techniques.

Engineering modification of the spray gun to better adapt it to spraying of pavement marking materials was considered outside the scope of this effort. One important such modification would be an adaptation that would allow good edge definition to be obtained with linear markings. This might be achieved by either changing the gun orifice geometry or by using metal delimiters that control the width of the spray. The modifications were not used in this effort, the flamesprayed lines shown in the Figures 2 have poor edge definition. It is therefore important to point out that this shortcoming is not inherent to the powdered resin compounds used in the study, or to the flamespray process itself, but is a result of using a spray gun designed for general coatings applications to evaluate pavement marking materials. As seen from the figures the powder coatings generally do yield a marking of acceptable opacity.

b) Durability of the compunds.

The period of performance of the present effort was too short to undertake a field evaluation of the durability of flamesprayed markings on concrete substrate. Durability, however, is a key characteristic of the performance of any pavement marking material. Outdoor exposure involves a variety of factors such as the effect of moisture, ultraviolet radiation and freeze-thaw cycles that have significant effects on the durability of coatings. However, durability is affected by the weathering characteristics of the marking material as well as by its propensity to undergo mechanical losses due to abrasion during use.

An estimate of the abrasion resistance of the material or the ease of removal of the marking material from the surface of the pavement can yield information that relates to durability. A preliminary effort was made to carry estimate the abrasion resistance of the coatings already flamespray applied onto the concrete substrates. But a high degree of variability in the results due to the unevenness of the substrate was apparent. The uneven coating on concrete substrate as well as the unevenness of the concrete surface itself prevents any meaningful evaluation of the properties of the sprayed-on films. (Outdoor exposure to measure the weatherability of these stripes should, however, be possible provided a long enough period of observation and testing is available). For the present exercise, measurements on laminates or thick films (~4 mm thickness) of the alkyd-based coating material (powder) specially molded for the test would provide more reliable information.

Compression molded sheets of the compounded resin powders were therefore used in a laboratory test on the ease of removal of material by abrasion . In the absence of an appropriate

standard test suitable for the purpose we devised a simple approximate test that would allow the relative abrasion resistance of these materials to be assessed. The simple test used here does not involve the abrasive environment or the mechanical damage to markings obtained under field conditions and is not intended as a simulation of the I-use conditions. It is rather a measurement that should correlate with abrasion-related losses obtained in the field, and is intended merely to compare the different formulations with one another.

In this test, thin plaques of the marking material (molded from powder) were abraded with a slowly rotating abrading wheel (0.25 inches wide) over a fixed period of time (10 or 20 mins.). This process removes the material as a fine powder from the surface, leaves a circular depression a few square cm in area on the test samples. A schematic diagram of the simple test device is shown in the figure 3 and essentially consisted of an abrading wheel mounted on an electric drill. The test device allowed the rotating wheel surface to be placed on the sample surface with about the same downward force against the sample. The quantity of the material was removed from each of the plaques, depends on the hardness and abrasion resistance of the material, The amount of material removed is gravimetrically estimated for each sample. To exclude any effects due to possible changes in abrasive effectiveness of the wheel itself during the course of the test, the series of samples were tested twice. They were tested once in the sequence shown in the Table 5 below and then in the opposite sequence, using a fresh abrading wheel each time. The material was removed by abrasion over about the same area of the sample in each case and the weight of the sample before and after the test was accurately measured using an analytical balance. The data obtained are summarized below in Table 5. Note that the samples were tested in the order indicated in column 1 and that the series A and series B samples are identical except that the latter was tested in opposite sequence.

For samples #1 through #4 both the weight fraction of the inorganic filler and the percentage of resin in the formulation are constant (about 40 prercent). But the composition of the resin fraction itself changes from about 10 percent to about 50 percent by weight of the polyamide in the resin blend part (the rest being the alkyd resin). In sample #4, for instance, the resin fraction is a 50/50 mixture of the alkyd resin with the polyamide material. The composition of the polymer resin fraction (that composes 40 percent of the formulation) has a marked effect on the abrasion resistance of the material. The data plotted in the figure 4 below shows a qualitative trend of increasing abrasion resistance under these test conditions with increasing fractions of the stronger polyamide material. No discernible difference in the ease of flame flame-spraying was noticed between these four sample types; they are all flamespray applicable as long as at least 4-5 percent of the composition is polyamide to allow the material to be adequately powdered. . The amount of polyamide to be used in the formulation is therefore determined by cost considerations and the abrasion resistance (and durability) of the marking desired.

Table5 : Data from the laboratory test on abrasion characteristics of the compositions

Sample	Duration (min.)	Initial Weight (g)	Final Weight (g)	Weight Loss (g)
1A	10	22.460	22.143	0.317
4A	10	18.974	18.884	0.090
7A	10	14.105	14.033	0.072
3A	10	19.329	19.160	0.169
2A	10	18.700	18.501	0.199
6A	10	17.700	17.577	0.123
5A	10	15.373	15.284	0.089
5B	20	15.387	15.227	0.160
6B	20	17.477	17.262	0.215
2B	20	19.375	19.022	0.353
3B	20	19.210	18.944	0.266
7B	20	14.032	13.892	0.140
4B	20	18.914	18.791	0.123
1B	20	21.842	21.379	0.463

A second variable studied was the effect of the fraction of calcium carbonate (and therefore the fraction of inorganic material) used in the formulation on the abrasion resistance of the material. Samples #7,#5 and #6 have weight fractions of calcium carbonate of 20, 30 and 40 percent, respectively. Therefore, these have correspondingly different weight fractions of the total resin in their formulations. But in each case, the composition of resin blend is about the same; 70 percent Sylvacoat alkyd resin blended with 30 percent of the polyamide resin. This constant blend ratio of the resins allows the data on these samples to be directly compared. As shown in Figure 5, these three samples show increasing abrasion resistance at higher fractions of the resin in the formulations. This is not surprising in that the presence of higher fractions of the resin allows better binding of the inorganic fillers limiting their removal by abrasion.

Note that the sample #3 with even higher percentage of calcium carbonate (~ 50 percent) also fits in well with the expected trend in abrasion resistance and is also included in the figure. This is the only sample in the set of samples #1 through #4 that can be directly compared to other samples included in the figure, as it has the same composition of the resin fraction (i.e. 30 percent of the resin fraction is polyamide.

1.6 Environmental merits of the technique.

A pavement marking material based on flamespray application of alkyd resin/polyamide blend-based coating would have a high degree of environmental compatibility compared to competing types of marking materials. Expressing the degree of environmental merits of any coating system even semi-quantitative terms is however, a difficult task. This difficulty arises not only because the relevant environmental attributes are not always readily quantifiable, but also because the relative importance of these attributes in determining the overall environmental desirability of a coating is not readily apparent. A recent study[1] attempted such a quantification

based on the expected utility values calculations using an empirical methodology. In this approach the engineering performance of a pavement marking material was quantified using six relevant measures while the environmental performance was assumed to be a function of three key attributes. These attributes were as follows.

i) The VOC content associated with the marking.[a_1]

ii) The potential toxicity of the volatile materials in the formulation.[a_2]

iii) Other safety hazards posed by the material .[a_3]

Where

.[a_1] = the quantity in pounds of volatile organic compounds (VOC) associated with a gallon of the material.

[a_2] = the hazard potential of the marking material expressed as the logarithm of the volume of air in cubic meters needed to dilute a pound of VOCs in the material to acceptable concentrations.

[a_3] = a rating between 0-5 based on other dangers such as the potential for fire hazard, the possibility of burns and high particle counts associated with the technique.

Each of the three measures expressed above in different units were converted to the common unit of expected utility by using a set of transformations. The exact mathematical transformations used for the conversion of these [a_x] values to utility [U_x] values is unimportant for the present purpose, except to note that for both the VOC level and potential toxicity U_x is a non linear decreasing function of toxicity and VOC content.

$$[a_x] \qquad [U_x] \text{ for } x = 1, 2, 3$$

The environmental performance of the marking is then the sum of weighted utilities, with the weights assigned by the perceived importance of the different attributes by a competent group of endusers. In the previous study, the environmental performance U_{env} was defined as follows.

$$U_{ENV} = k_1U_1 + k_2U_2 + k_3U_3$$

On the basis of this published methodology the present system of flame-spray applied alkyd resin formulation is qualitatively evaluated as having a high level of environmental performance. In most real situations the affected populations judge the toxicity of the volatile components in the pavement marking system, as well as the VOC load associated with the system to be far more important than the safety concerns. (i.e. $k_2 >> k_1 >> k_3$).

With the present 100-percent solids system there are no obvious volatile organic constituents that escape into the ambient air as no solvents are used in its composition. The only possible source of such volatile compounds might be the oxidative degradation or even pyrolysis of the polymer material during its passage through the flame. Given the very short residence times, however, degradation reactions of polymer are not expected during the process. This advantage has more to do with the engineering features of the spray system than the thermal resistance of the polymer. Therefore data relating to polymer powders typically used in flamespray coatings might

be used to illustrate the minimal amount of volatiles generated in the process.

The manufacturer of the flame-spray equipment has carried out testing with independent laboratories on volatile emissions encountered at the operator position while the equipment ios in use. The volatile compounds detected with the test polymer used (ethanol, acetone and acrolein) were at levels of less than 0.05 ppm (orders of magnitude below the maximum permissible levels suggested by OSHA. (Maximum level for ethanol and acetone is 1000 ppm while that for acrolein is 0.1 ppm). A fourth volatile compound, methacrylic acid, was found at the slightly higher level of about 4 ppm (still several times below the permissible level). Methacrylic acid residue is expected in the breakdown of copolymers containing methacrylate or methacrylic acid. The present system would not produce significant methacrylic acids as volatiles.

The values of [a_2] and [a_3] for the system are both therefore close to zero, which would make this an exceptionally attractive candidate compared to any paint, any two part system that uses a low molecular weight cross linking material that is toxic, or even tape that uses adhesives. The environmental benefits are at worst the same as that for spray applied thermoplastics, except that the safety disadvantages of maintaining and transporting large volumes of molten plastic is avoided.

3.0 Conclusions and Further Work

3.1 General Conclusions

The commercially available alkyd resins used in thermoplastic pavement marking materials can be formulated as a good flame-spray applied thermoplastic marking powder material. To be able to do so, however, it is important to

a) compound the marking material without glass beads (beads being dropped on to the marking); and

b) to incorporate a suitable plasticizing polymer (in this case a polyamide material) to obtain effective grinding characteristics to obtain the requisite particle size and to have adequate melting characteristics in the flame. The fraction of the polyamide needed is small (as low as 10 percent) but the blend needs compounded along with the other additives that typically go into such formulations.

The compositions are easily sprayable using conventional gravity fed-guns flamespray provided the proper average particle size and distribution is achieved in the powder coating material. While ambient temperature grinding was used for the purpose in the present work, cryogenic grinding might also be profitably employed with large volumes of resin.

While the durability of the flame-sprayed coating film cannot be assessed without long-term exposure experiments, an empirical measure of abrasion resistance gives some indication of their general mechanical integrity. Based on the empirical findings the ease of abrasion loss of the coating system was clearly related to the fraction of the polyamide in the resin blend used in

formulating the powder. The abrasion resistance is therefore controllable to some extent by changing the formulation. However, these conclusions were reached by testing comptression-molded as opposed to flamesprayed samples.

In general, the environmental compatibility of a flanmespray applied thermoplastic is believed to be superior to other types of pavement marking systems with the exception of spray-applied conventional thermoplastics. The data is not available at this time to compare the life-cycle cost effectiveness, the durability and the engineering performance of the two thermoplastic systems.

1.2 Suggestions for Further Study.

The results discussed in the report provides general feasibility of designing a flame-spray applicable pavement marking composition based on low-cost alkyd resins. It is a 100 percent solids, environment-friendly marking system that can be applied using existing equipment minimally modified to improve edge definition. However, considerable developmental work and economic assessment needs to be undertaken prior to commercialization of the new marking system. The major efforts needed are in the following areas of research.

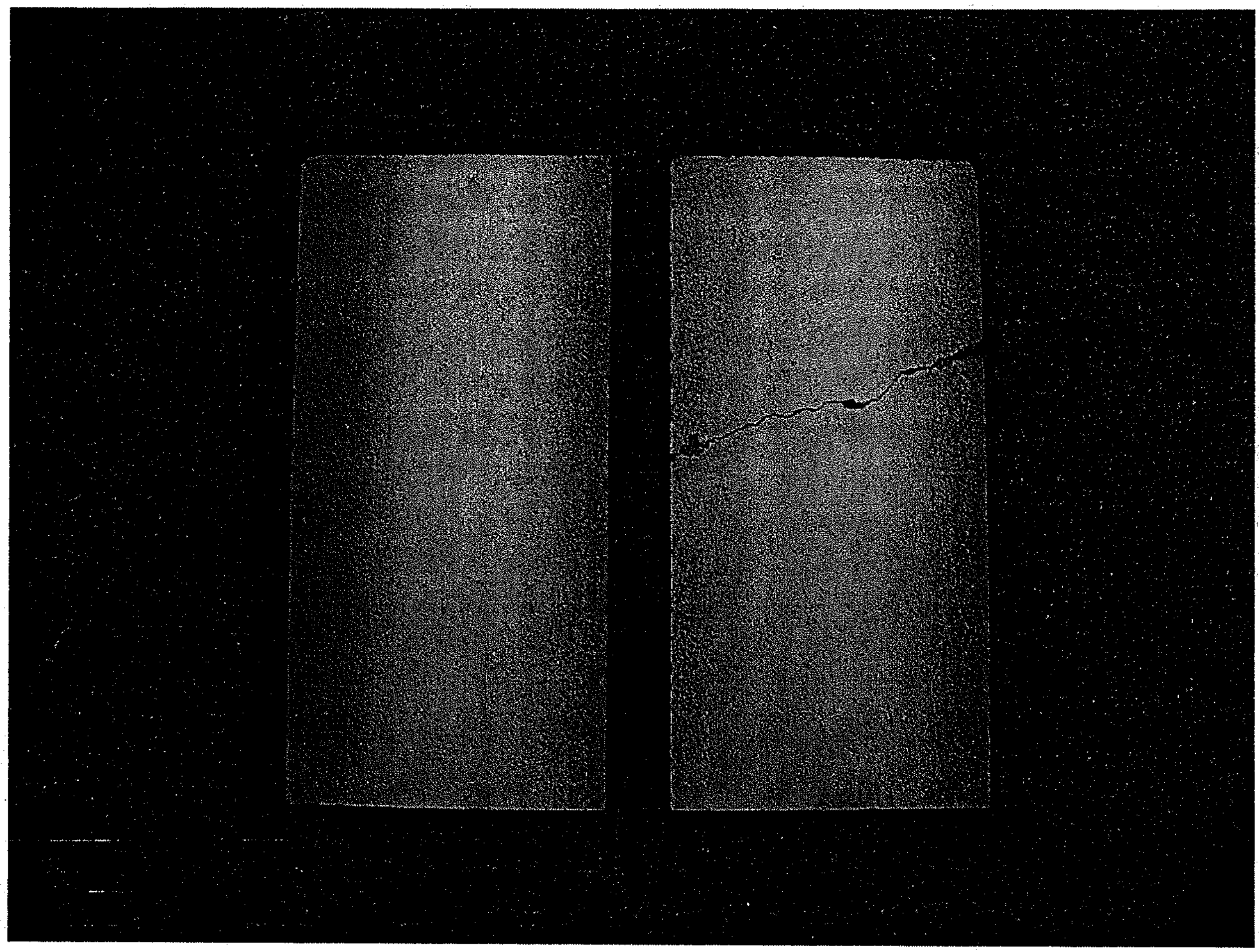
a) Identifying other polyamides or other synthetic resins that might be able to modify the melt characteristics and grinding behavior at a lower cost or at a lower level of incorporation into the alkyd resin. This involves a systematic study of resin blends to identify suitable candidates.

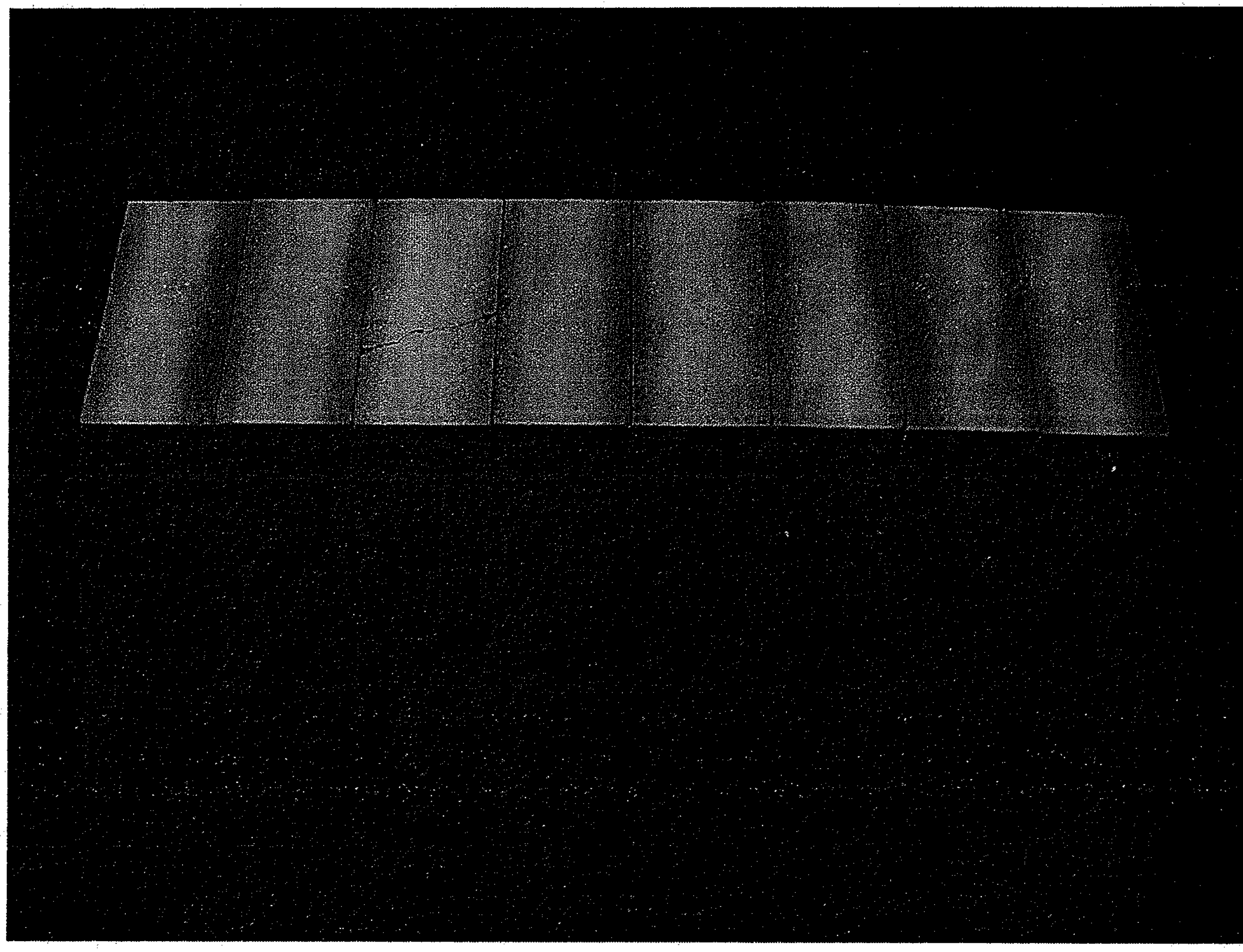
b) Optimization of spray characteristics best suited for the selected blend by selecting proper flame temperatures and residence times.

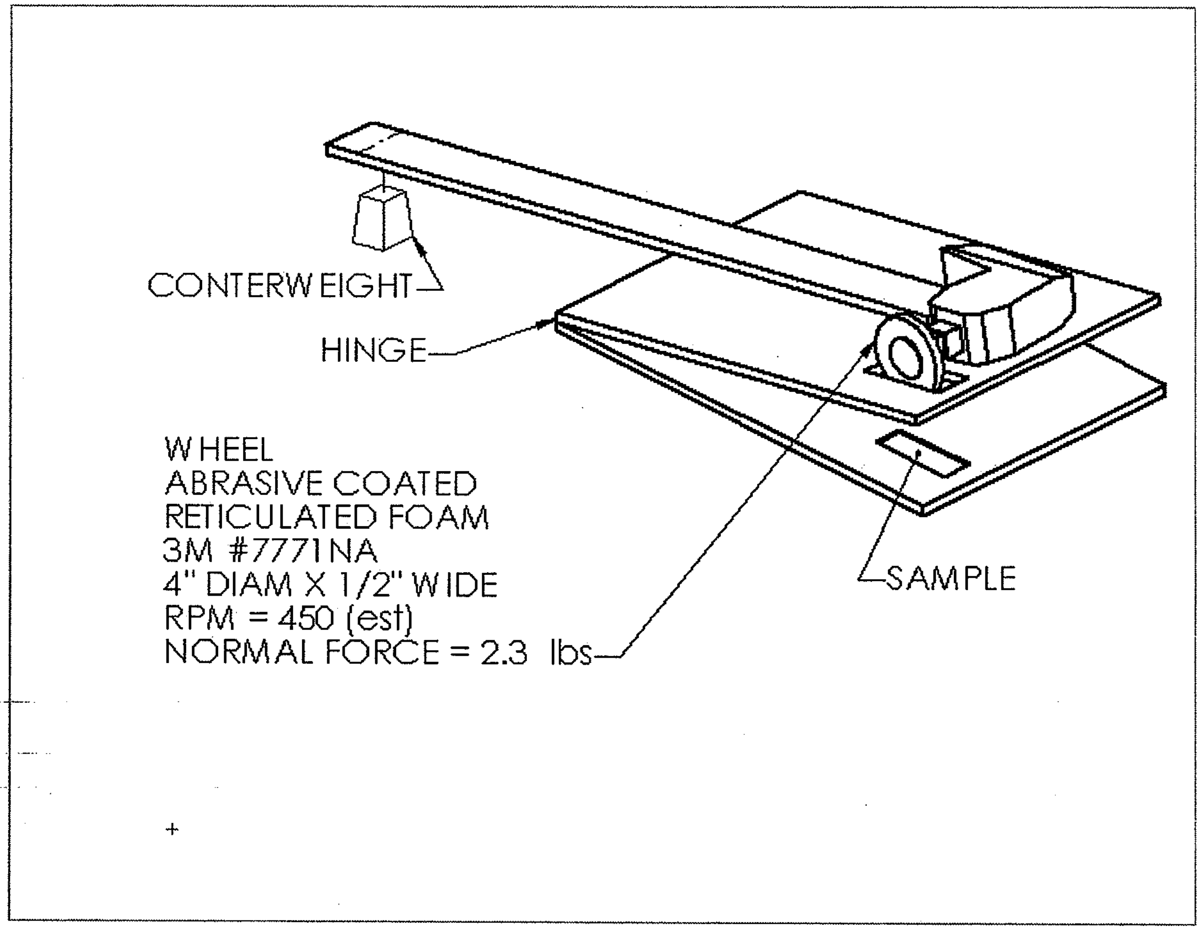
c) Demonstration of the drop-on placement of glass beads in a single operation along with flame-spray application.

d) Improvement of edge definition to acceptable levels using modifications to the spray gun.

e) Analytical studies to demonstrate the lack of significant levels of volatile emissions during the application of the resin by flame spray techniques.






CONTERWEIGHT
HINGE
WHEEL
ABRASIVE COATED
RETICULATED FOAM
3M #7771NA
4" DIAM X 1/2" WIDE
RPM = 450 (est)
NORMAL FORCE = 2.3 lbs
SAMPLE