

New Hampshire
DOT
Research Record

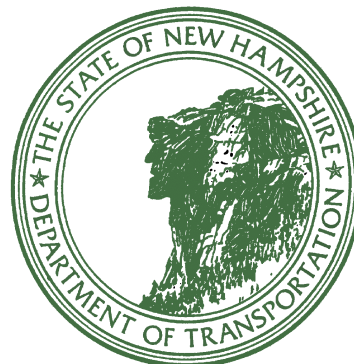


Waterborne Traffic Paints – A Study for
the Potential Improvement in Durability,
Drying Time, and Cost-Effectiveness

Final Report

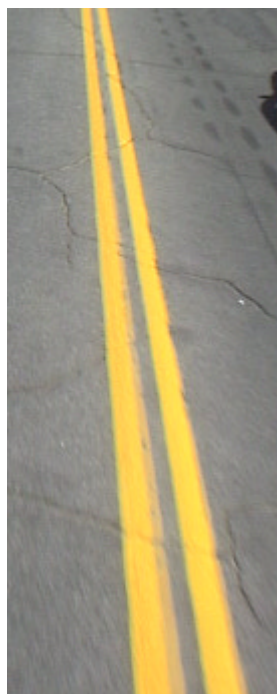
Prepared by the University of New Hampshire, Advanced Polymer Laboratory for the New Hampshire Department of Transportation, in cooperation with the U.S. Department of Transportation, Federal Highway Administration

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16. Abstract This report analyzes possibilities for developing an alternative to the present technology of 100% acrylic waterborne (WB) paints used for road delineation. The current market situation is briefly reviewed, and alternatives considered. The requirements of an alternative technology are: <ul style="list-style-type: none"> • Similar or lower cost in terms of price/foot/year • Longer lasting performance • Similar or better application constraints, namely "drying time" The report suggests interim steps to improve the cost-effectiveness of existing technologies through performance-based standards. It then goes on to determine what resources would be needed to bring to "proof of concept" stage an alternative coating that would meet the stated requirements. The final recommendation of this report include the revision of the procurement specification for waterborne traffic paints, the development of a test deck for traffic paints in NH, a detailed and careful R&D program to develop new retro-reflective beads and new waterborne paints containing hybrid polyurethane-acrylics binders prepared by mini-emulsion polymerization.					
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Waterborne Traffic Paints

A study for the potential improvement in drying time and cost-effectiveness



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Introduction

This report analyzes possibilities for developing an alternative to the present technology of 100% acrylic waterborne (WB) paints used for road delineation. The current market situation will be briefly reviewed, and alternatives considered. The requirements of an alternative technology are:

- Similar or lower cost in terms of price/foot/year
- Longer lasting performance
- Similar or better application constraints, namely "drying time"

The report suggests interim steps to improve the cost-effectiveness of existing technologies through performance-based standards. It then goes on to determine what resources would be needed to bring to "proof of concept" stage an alternative coating that would meet the stated requirements.

This report is not an exhaustive review of traffic paint technology; this type of review was very well done in 1993/1994 by the FHWA in a comprehensive report "Roadway Delineation Practices Handbook"¹. It also is important to understand that this report is focused on the particular needs of the Department of Transportation of the State of New Hampshire given their current practices. However, most of these same considerations should apply to other northerly states.

Background information

Traffic paints regulation

Environmental regulations issued by the US Environmental Protection Agency have required dramatic reduction of the acceptable level of Volatile Organic Compounds (VOC) in traffic paints during the 1990's. Prior to the EPA standards established in April 1995, the majority of the coating paints were alkyd paints with a VOC concentration greater than 450 g/l. The recent regulation introduced an upper VOC concentration of 150g/l. Current 100% acrylic WB paints have VOC's between 98 and 120 g/l, and 100% WB acrylic traffic paints now largely dominate the market.

Market considerations

With over 4,000,000 miles of roads, the traffic paint market is a \$300 million dollar per year business². This market varies widely across the US because of weather and traffic requirements. While the northern states have to repaint 80 to 90% of their state roads and highways every year, at an applied cost of 4 to 6 cents/foot for their waterborne acrylics, the more southern states have more options. Southern states have found safe

and possibly cost effective alternatives to 100% acrylic paints, namely raised reflectors, thermoplastic paints and epoxy paints. All three technologies are more expensive, but have long lasting performance in those warmer climates. Raised reflectors dominate California, but those devices are incompatible with snowplows (the blades tear them off the pavement). Thermoplastics are very expensive to implement with an applied cost of up to 60 cents/foot, but are expected to last 3 to 5 years. Their principal advantage is that they do not contain VOC's. Finally, epoxy paints are also expensive with an applied cost of 40 cents/foot. From a strictly financial point of view WB acrylics are certainly more attractive³. Table 1 summarizes the price differential between the three main paint systems: 100% acrylics (waterborne), thermoplastics and epoxy paints.

<i>Paint system</i>	<i>100% WB acrylics</i>	<i>Thermoplastics</i>	<i>Epoxy's</i>
Applied cost (\$/foot)	0.04 to 0.06	0.4 to 0.6	0.4 to 0.45
Expected life (years)	0.25 to 1	3 to 5	1 to 2
Cost / year (\$/foot/year)	0.04 to 0.24	0.08 to 0.20	0.22to 0.4

Table 1. Price comparison of 3 dominating paint systems.

In the state of NH, WB acrylics are predominantly applied, with the exception of pedestrian crossing sections and very high traffic areas (city intersections) where thermoplastics are used. Because of the harsh winter weather in NH, roads have to be plowed with intensive use of salt and sand. Those conditions are very "destructive" for the acrylic traffic paints. In a first step the light reflective glass beads are torn off the coating, then the traffic over those lines in combination with residual sand and salt wear down the remainder of the paint strips. In most areas of medium to high traffic, the paint stripes no longer meet the safety requirements of FHWA by the end of the winter season.

Technology background

Waterborne polymer binders are a prime choice for traffic paints. They offer the following advantages over solvent-based paints, thermoplastics and epoxies:

- Absence of environmentally unfriendly solvents
- Good water resistance when completely dried
- Safe for traffic personnel
- Easy application through the use of current traffic paint equipment

Typical paint composition.

Traffic paints are composed of several chemicals: polymer binder (also called vehicle) (15% on average), pigment (on average 50%), solvent, coalescing agents, stabilizers, viscosity adjusters (15% on average) and water (30% on average). Each chemical brings a specific and critical property to the overall performance of the coating:

- Polymer binder: provides paint cohesion, weather resistance, mechanical elasticity
- Pigment: provides color
- Filler (can be a pigment): provides some of the wear resistance, hiding (opacity), some of the brightness, but mostly reduces price per pound.
- Water: provides low viscosity during transport and application, is completely evaporated when the film dries. This is the best, environmentally friendly, solvent.

- Organic solvent (usually methanol) and other coalescing agents: improve film formation, and consequently provide greater wear resistance. Solvents contribute to the VOC content; coalescing agents typically remain in the film.
- Other additives in small amounts provide light resistance, storage stability, and biodegradation control.

This report focuses on the polymer binder because it determines most of the properties of the final film and is the second most expensive component of the formulated paint. The price per dry pound of the polymer binder is higher than the price of any of the fillers. Consequently paint formulators always try to minimize the amount of binder present in the paint in order to lower their cost and be more competitive, even at the expense of performance. This practice is detrimental to the cost effectiveness of the paint.

Conventional water based polymer binders used for paint formulation are made through the emulsion polymerization⁴ of mixtures of acrylate, styrene and/or butadiene monomers. The simplified structure of a formulated paint is shown in figure 1 in its wet (before application) and dry (after application) states.

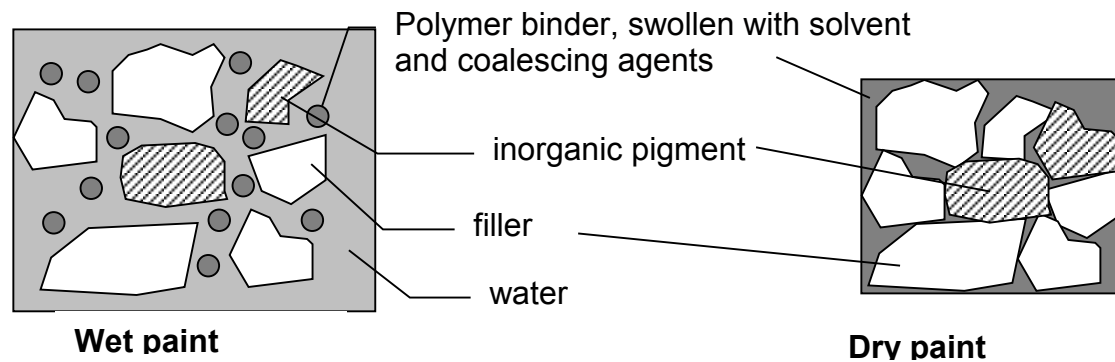


Figure 1. Waterborne paint structure in wet and dry states.

Finally, glass beads are mechanically projected on the freshly applied paint film to provide the light reflection that is essential for night driving, as illustrated in figure 2. The beads are significantly larger (5mm) than the thickness of the paint film (4mm), which ensures that the beads are “raised” above the film. The adhesion of the beads to the film is an important issue, and is usually described as bead retention. A small section of this report addresses some possibilities to improve bead retention.

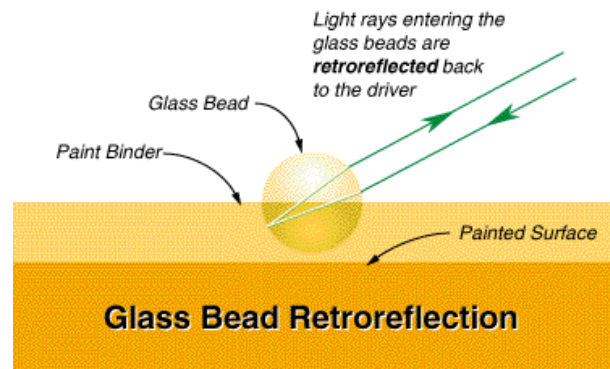
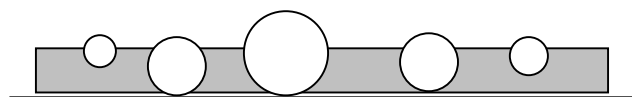


Figure 2. Retro reflective glass beads at the surface of traffic paints.

The development of paint typically involves two elements:

- Development of a polymer binder
- Formulation of the paint

Traditionally, most paint formulation effort has been focused on adapting classic polymer binders to the specific requirements for use on roads. The formulation companies are traditionally small and medium size companies, while the polymer binder manufacturers are very large corporations (e.g., Rohm & Haas, BAF). There are nearly 7500 paint formulators, and fewer than 20 polymer binder manufacturers.

A review of current waterborne traffic paint specifications reveals several weak points:

- Restrictive material definition: they require 100% acrylics. This does not allow manufacturers to pursue higher performance paints that contain polymers other than acrylics.
- The current maximum VOC content of 150 g/l is very high and should be reduced to anticipate up-coming EPA regulations.
- No clear lower limit for binder content is stated. This could result in procurement of paint that meets the established standards yet has poor long term durability.
- Faster drying acrylics have lower glass transition temperatures (Tg's) than "normal dry", but do not weather as well. They also contain the maximum allowable 150g/l VOC content in the form of methanol.

These specification weaknesses result from the difficulty in finding the best compromise between performance and cost-effectiveness. While in the past all requirements were composition driven, the current trend is to include a performance based requirement. Retention of composition standards during transition to performance based standards undermines the process by limiting improvement in some areas (such as binder composition).

Potential for drying time improvements

General considerations

Drying time varies significantly with weather conditions (temperature and humidity). Both limit the window of time during which the DOT and contracted applicators can apply traffic paints on roads. Figures 3 and 4 illustrate the influence of temperature, humidity and wind condition on the drying time of two different WB acrylic paints⁵.

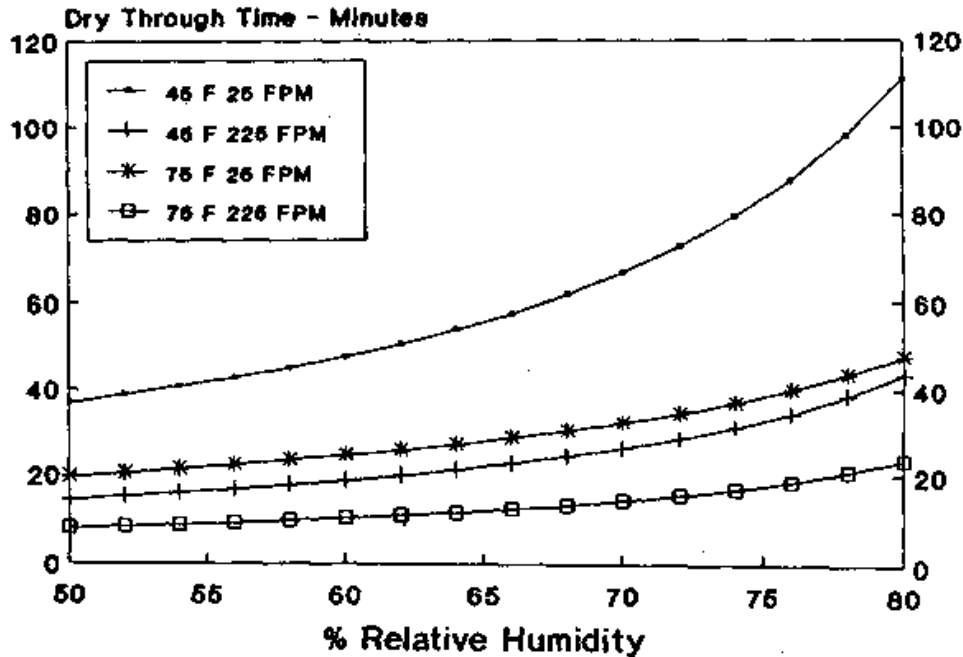


Figure 3. Drying time for conventional WB acrylic paint as function of relative humidity for two wind speeds and two temperatures.

For a conventional WB acrylic (figure 3), drying time can vary between 10 minutes (warm, dry, breezy) to 2 hours (cold, wet, non breezy).

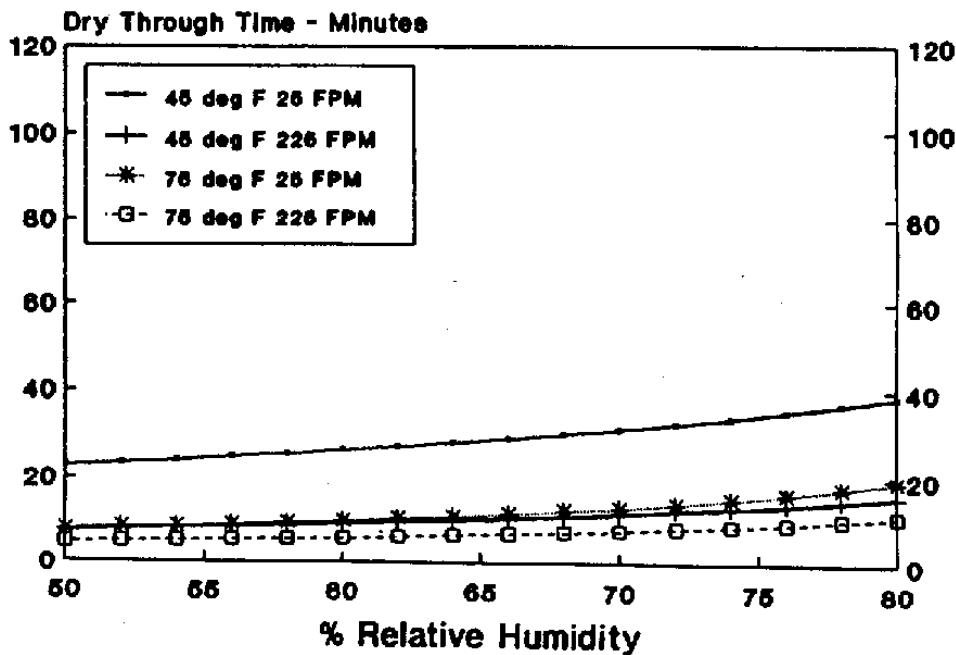


Figure 4. Drying time for fast dry WB acrylic paint as function of relative humidity for two wind speeds and two temperatures.

For a fast dry WB acrylic (figure 4), drying time can vary between 5 minutes (warm, dry, breezy) to 40 minutes (cold, wet, non breezy). For these products the influence of temperature is minimal. On the other hand, the influence of wind (ground air speed) is

dramatic, reducing drying time by a factor of 3 when going from 26 ft/min (0.1 miles/hr) to 226 ft/min (1 miles/hr).

Several potential solutions are briefly described here, and some of them will be analyzed in more detail in later sections of this report.

1. Direct heating of the freshly applied coating: this concept involves the development of a “train” of infrared heaters that would follow the paint striper truck and heat up the film to increase its drying rate (hence evaporate water faster).
2. Direct air-drying of the freshly applied coating: this concept consists of blowing dry air at high velocity over the freshly painted traffic line (artificial wind created by following vehicles)
3. Use of high solid mini-emulsion (70% Solids Content (S.C.) Acrylic): mini-emulsion is a polymerization technique offering the same benefits as high solid conventional emulsion, but with the potential for even higher solid content. A formulated paint using such binders has lower water content (at constant viscosity) and can consequently dry faster. This technology is still relatively immature, but is the subject of intense research and development.
4. Destabilizing agent (separate spray): by spraying on top of the latex a water solution of high ionic strength, the paint can be destabilized to form a cheese-like paste. The resulting product can dry significantly faster. Drying agents also can be sprayed on top of the paint. Highly hydroscopic polymer (polyacrylamid or polyacrylic acid – as in baby diapers) can attract a large fraction of the water present in the paint to the surface of the coating. This top polymer layer would wash off the pavement and degrade naturally. Inadvertently sprayed personal vehicles could be simply cleaned with a hose.
5. Dry paints. Dry paints are a fast growing segment of the industrial coating market. They can be made by various techniques and can be applied either by a dry spray or with a super critical CO₂ spray. Using such technologies for traffic paint would represent a significant leap forward. Advances in infrared curing can be combined to provide excellent films.

Table 2 summarizes these techniques and categorizes (L-low, M-medium, H-high) their benefits, technical difficulties and added cost to the applied paint.

<i>Potential solution</i>	<i>Benefits</i>	<i>Risk / difficulty</i>	<i>Added cost to product</i>
Direct heating of the painted strip	M	H	H
Direct air drying of the painted strip	H	M	H
High solid mini-emulsion (70% S.C. Acrylic)	M	M	M
Destabilizing or drying agent (separate spray)	M	M	M
Dry paints (with post curing or CO₂ plastisation)	H	H	H

Table 2. Risk benefit analysis of various solutions to reduce paint drying time.

Unfortunately there is no (potential) solution offering a low added cost with high benefits and low risk/difficulty.

Direct heating

In order to be effective, direct heating of a wet applied coating must avoid rapid dissipation of energy into the ground (asphalt). To assess the potential for this approach, heat transfer theory was applied to a model “air/paint/asphalt” system. Because of the symmetry of the delineation marking, (several miles long, 4-6 inches wide, 5 inches or more of asphalt), this problem was considered to be one dimensional, going from the surface (i.e., paint film) 5 inches into the ground. The surface of the film is exposed to heat loss by convection, with “zero” wind condition. The ground extending below the 5 inches of asphalt is considered to be a heat sink, or in other words, that it can extract heat without limitation while remaining at a constant temperature. The geometry of the model system is represented in figure 5.

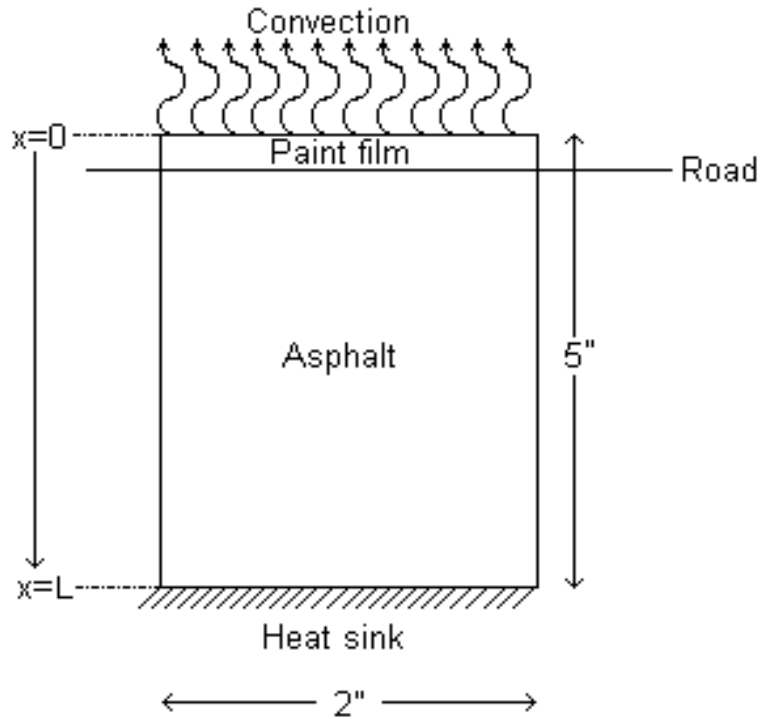


Figure 5. Simplified paint/pavement for heat transfer modeling

The one-dimensional transient heat transfer equation⁶ was solved numerically⁷ in “C” language⁸. Because of the relative complexity of the model, only the results are given here. The actual details of the modeling are given in the appendix. The large set of equations was solved for a specific set of conditions, namely: the asphalt was assumed to be a mixture of stones and rubber; the ground temperature was assumed to be 25C (reasonably warm); the film was assumed to be applied very hot (60C); and it was assumed that no wind cooled the surface. Overall, the model is set to represent the conditions under which the least amount of energy would be lost.

The first solution considered that no heat was provided to the wet film (direct heating turned off or current technology). Figures 6 and 7 represent the result of this simulation. Each graph represents the temperature profile of the film at different time increments from time equal 0 (coating just applied) up to 30 minutes, in 3 minute time intervals.

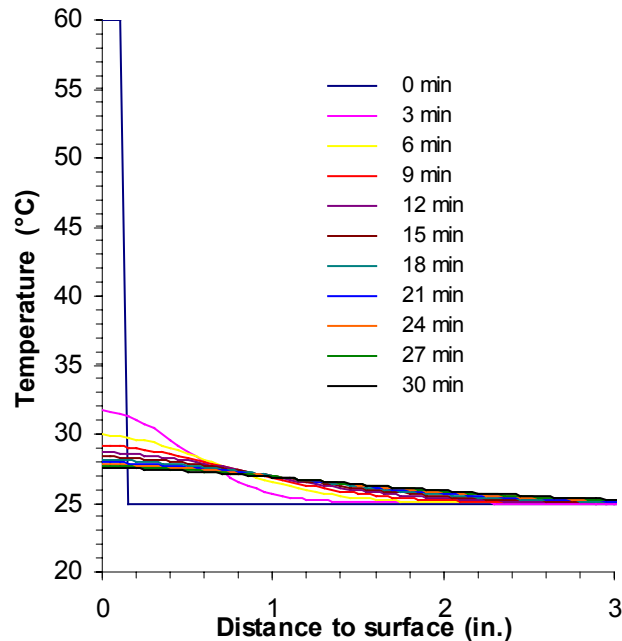


Figure 6. Temperature profile without internally generated heat in. Large temperature scale.

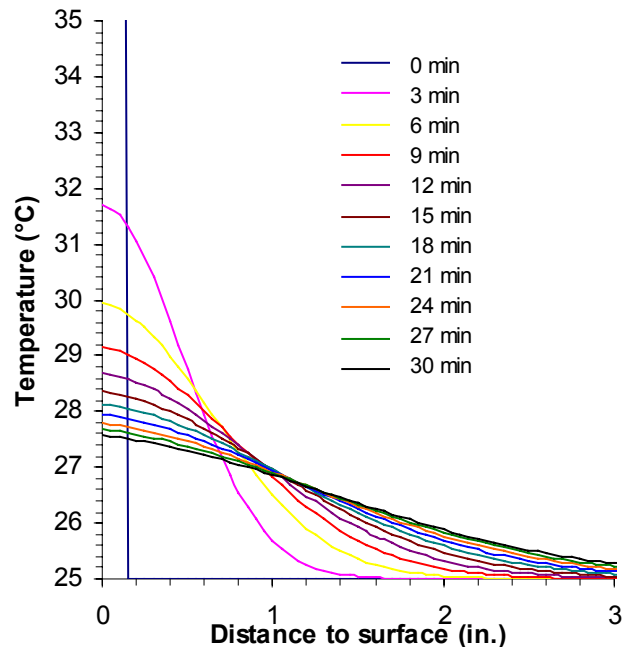


Figure 7. Detail of figure 6. Small temperature scale.

Figure 7 is similar to figure 6 with the temperature scale expanded from 20-60C to 25 to 35C to separate the curves. One can observe that after 3 minutes only the first inch of the system remains above ground temperature with a maximum of only 32C. After 30 minutes, the surface temperature reaches 27.5C. Those temperatures are certainly not high enough to enhance the drying rate of the film. In reality the temperature would be even lower, due to the cooling effect of water evaporation and surface air speed.

The next simulation involves the incorporation of a source of heat. From a modeling point of view, it does not matter if the heat is introduced by an infrared source or by a

chemical exothermic reaction within the film. In figures 8 and 9, temperature profiles of the system are again reported at 3 minute intervals.

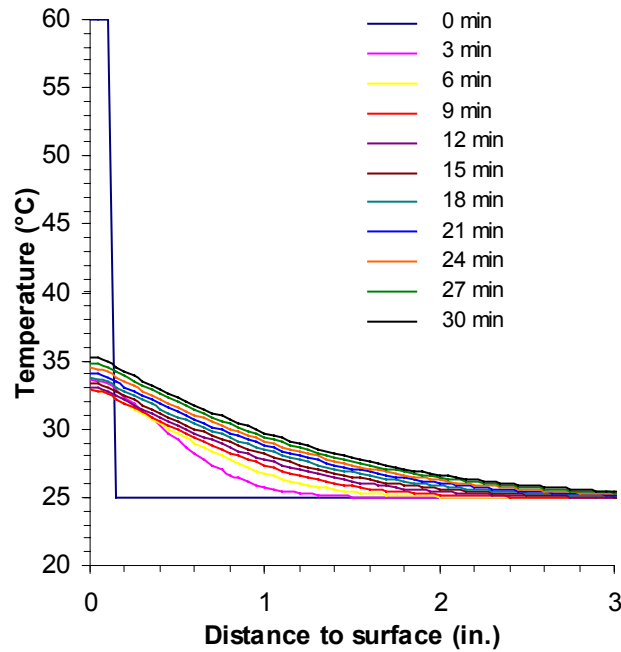


Figure 8. Temperature profile with internally generated heat in seconds. Large temperature scale.

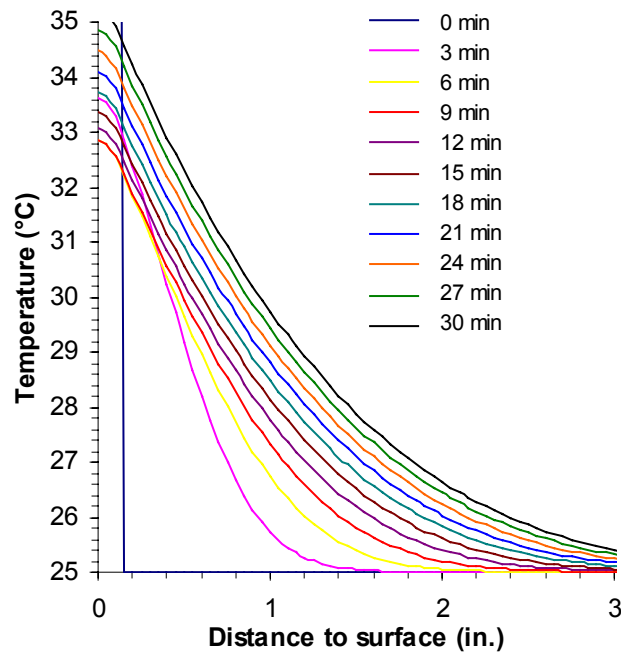


Figure 9. Detail of figure 8. Small temperature scale.

This time the top layer remains warmer, with temperature increase being noticed up to 3 inches into the asphalt. But the film temperature remains between 35C and 33C, again not enough for an enhanced drying rate.

This theoretical study shows that direct heating of the film would be utterly inefficient, because the heat is “lost” into the first inches of the asphalt. This solution is not realistic.

Direct air drying

Encouraged by the wind effect reported in the literature, we considered use of an artificial source of dry air for humid-windless days. Before considering the mechanical challenges involved with such a setup we quantified the drying-time reduction obtained by the air-blower concept. We used a Perkin-Elmer thermo gravimetric analyzer (TGA) to quantify the drying process under two conditions of nitrogen flow (representative of dry air). We applied a low and constant temperature of 5C to report data under adverse conditions (cold day). We used a fast dry yellow WB acrylic paint, and recorded the drying rates of figure 10.

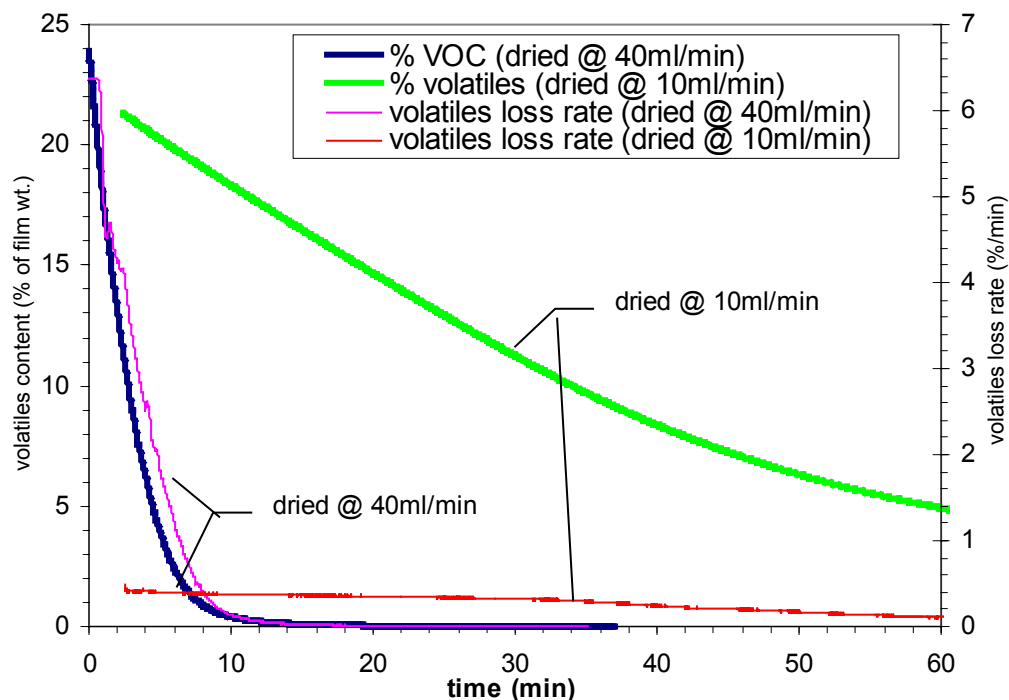


Figure 10. Drying rate of paint under 2 different air flow

Figure 10 represents the level of dryness (Volatile Content) on the left “y” axis (thicker lines), and the drying rate on the right “y” (thinner lines). One can observe a dramatic effect of the nitrogen flow on the drying rates. While at 40ml/min the paint is dried in 10 minutes, it takes close to 2 hours to dry the same film with a nitrogen flow of 10ml/min.

Those results are useful only in terms of comparison to each other. The films we used in the instrument (TGA) are particularly thick (2mm), which is not the case of the traffic paints applied on New Hampshire's roadways. Nonetheless the result stands that a significant increase in air velocity (4 times) can reduce the drying time by a factor up to 8.

Applied to standard “fast dry” reported dry through times of 15 minutes or less, we could conceivably reduce that dry-through time to 2 minutes.

Current paint strippers apply paint at a nominal speed of 12 miles/hour. An “air-dyer truck” following the stripper at a safe distance of 100 meters at the same nominal speed

would have to span 322 meters in order to supply dry air for 2 minutes. A single truck indeed cannot accomplish this, but a combination of several trucks trailing each other could be in effect a 50 meter “drying” train. This solution is consequently attractive only for extreme conditions, such as striping campaigns on large highways where a large convoy of trucks is necessary to insure traffic safety. This process also eliminates the need for a striping crew to install and retrieve safety cones, which is in itself a dangerous practice for the crews. The variable cost of such a solution is mostly related to the wages of the striping crews (already in place). A significant fixed cost would have to be met to purchase the drying trains. Those would be simply attached to standard DOT pickup trucks. An air compressor with a water condenser would provide the dried compressed air at minimal cost.

Thus, this option might have potential for certain high-use applications, but is not likely to be useful for the large numbers of lower volume roads and highways.

High solid content miniemulsion

Batch miniemulsion polymerization.

An alternate solution to obtaining faster drying paints is to manufacture a binder with less water; hence requiring less time to evaporate all the water. The miniemulsion polymerization (mEP) is a very powerful technique to prepare complex waterborne polymeric binders. This process is at its best in applications involving the dispersion in water of organic molecules having very poor water solubility. An excellent review of this field has been done recently by David Sudol and Mohamed El-Aasser⁹. At UNH researchers have been working on this emerging technology and have made significant progresses in the preparation of high solid content miniemulsions. Emulsions with polymer content as high as 70% have been produced on a regular basis. Traffic paints formulated with binders of such high solid content can provide significantly faster drying times.

To obtain a miniemulsion, a source of high shear is required. Equipment such as sonicators, microfluidizers and homogenizers are particularly efficient at creating emulsion of monomers with very small droplets. The usual size of these droplets is between 50 and 500 nm. To greatly enhance the stability of these droplets, a hydrophobic molecule is necessary. A hydrophobic molecule such as hexadecane will drastically inhibit the coalescence of the emulsion (by Oswald ripening). This process is illustrated in Fig. 11.

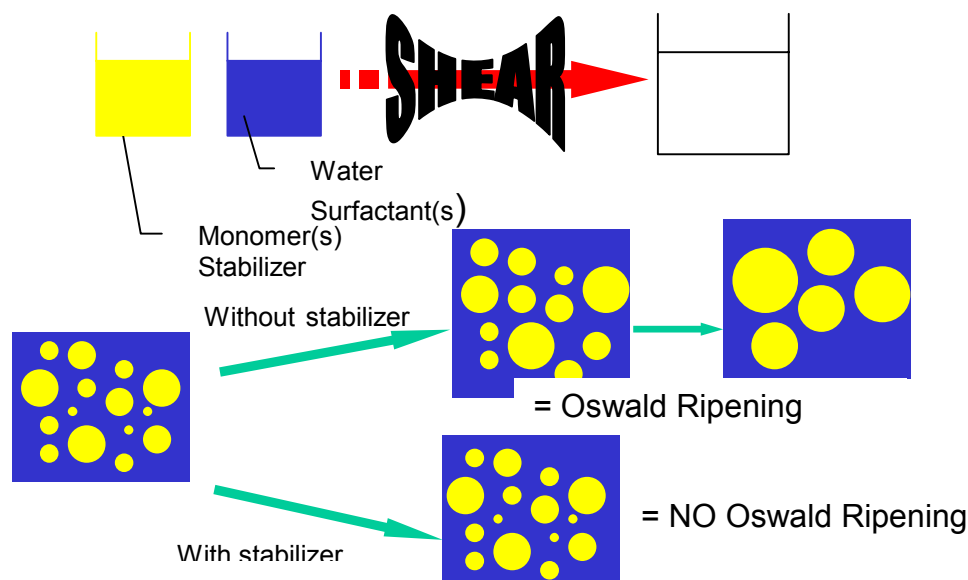
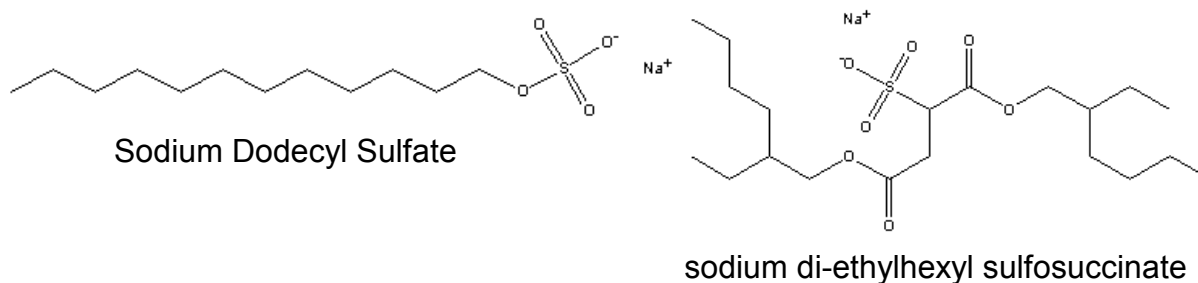


Figure 11. Simplified process to prepare a miniemulsion.

To prepare a high solid content miniemulsion, UNH researchers used a combination of two surfactants, one of great surface activity (strong stabilization of emulsions), such as Sodium Dodecyl Sulfate (SDS), and another surfactant having particularly high water mobility (fast stabilization), such as sodium di-ethylhexyl sulfosuccinate. The combination of those two surfactants was found to be particularly effective at stabilizing miniemulsions at monomer contents up to 50% in weight. The combination of a dynamic surfactant (di-ethylhexyl sulfosuccinate), a high surface activity surfactant (sodium



dodecyl sulfate), and a high-energy sonication, can generate miniemulsions of particle size averaging 100nm.

To obtain monomer content greater than 50%, It was necessary to use a continuous sonicating cell coupled with a re-circulating pump to insure greater "stirring" within the sonicator cell. After sonication, there is a very viscous emulsion of monomers in water, with consistencies similar to

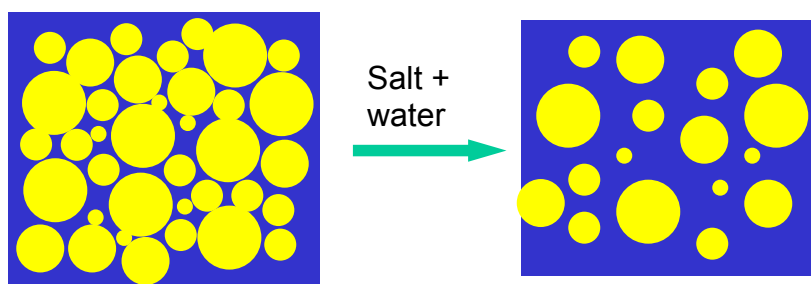


Figure 12. Illustration of the effect of adding salt to a high monomer content miniemulsion.

pastes and having very broad particle size distributions. Unfortunately such viscosities are not appropriate for polymerization and later applications. An original solution to this issue was achieved by creating a very high monomer content emulsion of high viscosity and adding small amounts of salt in water. This operation greatly reduced the viscosity by reducing the electrostatic double layer, as illustrated in figure 12.

The viscosity reduction is evident in figure 13. A miniemulsion containing 70% monomer has been diluted with water (top curve) and with water plus 10 weight % sodium chloride salt (bottom curve). When adding the salt solution, a reduction of only 4% in monomer content is necessary to obtain viscosities as low as 200cp, which is adequate for most polymerization reactors and pumps.

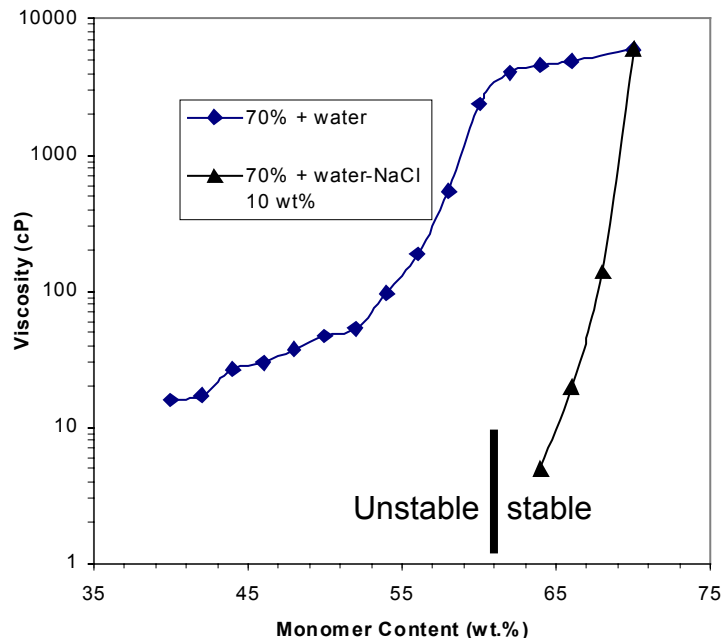


Figure 13. Viscosity reduction by addition of salt.

The polymerization of these miniemulsions is done in a batch mode by simply adding a water-soluble initiator such as sodium persulfate. Most monomer “minidroplets” capture a radical and polymerization occurs at a particularly high overall rate. The small average particle size of the miniemulsion provides not

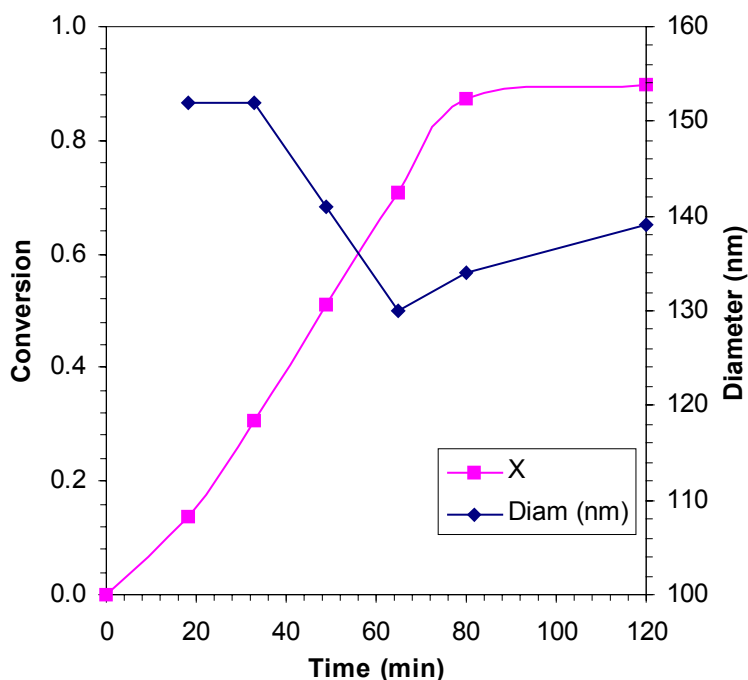


Figure 14. Polymerization of a miniemulsion of styrene. Monomer conversion and average particle size diameter as a function of time.

only great shelf stability, but also low coagulum levels and high “droplet versus new particle” nucleation ratios. As mentioned by Miller et al.¹⁰, renucleation is still present in mEP.

A typical miniemulsion polymerization of styrene is presented to illustrate the results. The recipe and polymerization conditions are assembled in table A1 of the annex section. Figure 14 represents the conversion of the monomer (styrene) into polymer (polystyrene) as a function of time. One can see that most of the polymerization occurs within

1 ½ hour. On the same figure the average particle diameter is plotted (right axis) and only small variations from 155 to 130 nm are observed during the polymerization. This near-constant size illustrates the polymerization of each monomer droplet. One of the direct consequences of such a phenomenon is the possibility of incorporating a dye into the binder matrix. The dye could be a UV dye to enhance night vision, or UV sensitive molecule to provide crosslinking, or a molecule to provide a specific response to a particular environmental input. For example, a molecule that changes color below freezing could be incorporated into the binder.

Continuous miniemulsion polymerization.

Because of the fast polymerization rate, standard batch polymerization reactors are not capable of extracting the heat associated with the polymerization. The classic solution in industry has been to use semi-batch (or semi-continuous) processes. In these processes the monomer is added “slowly” to the reactor to limit the polymerization rate. Unfortunately, such an approach is not possible with miniemulsions; it is necessary to remain in a batch operation mode. The best solution to this engineering problem is to design a reactor having a very large surface area to provide maximum heat exchange between the reactive emulsion and the cooling system. At the University of New Hampshire researchers have focused on demonstrating a continuous process using a tubular reactor. In such a reactor the miniemulsion is fed continuously at one end of a tube and continuously polymerized inside the tube. Such a process offers numerous advantages such as low operating cost, low capital investment and high output.

To further demonstrate the industrial relevance of the mEP process, several research laboratories have been developing continuous processes¹¹. At the University of New Hampshire, a simple experimental setup has been built. It involves three rotating piston pumps, an ultrasound flow

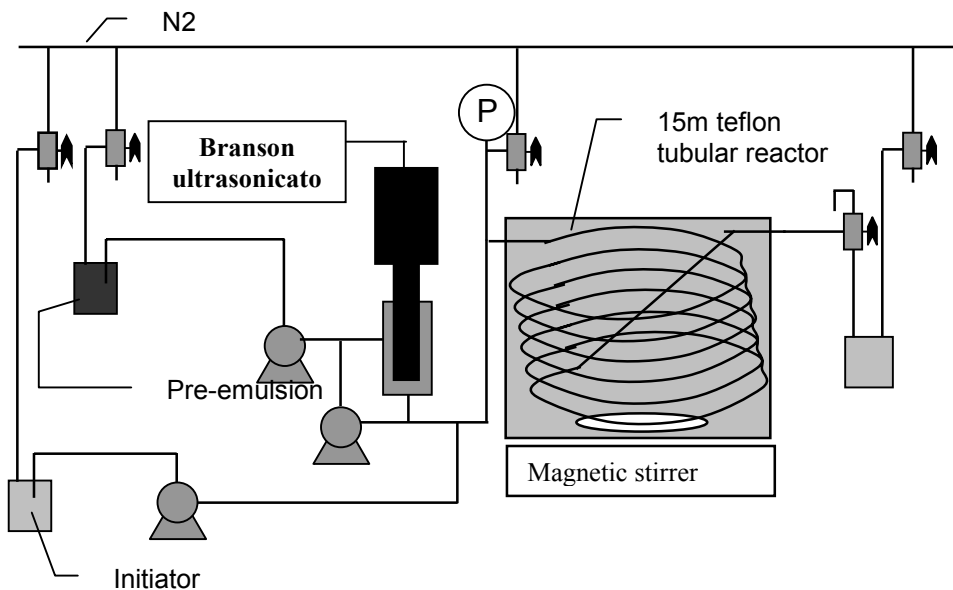


Fig. 15. Continuous miniemulsion polymerization setup.

cell and a modified tubular reactor. Figure 15 outlines the principles of the setup. Mixing of the aqueous initiator solution after ultrasonication was found to work best. It also was found that using a “recycle” loop around the continuous flow cell of the sonic probe was critical to maintaining a homogeneous miniemulsion. The use of rotating piston pumps allowed mild pressurization of the reactor and pumping of high viscosity miniemulsions. Strong cooling of the flow-through cell is absolutely necessary.

To demonstrate the polymerization mode occurring inside the tubular reactor, the same recipe was run in a classic batch reactor and in the continuous tubular reactor as described in table A3 and A4 of the annex. The results showed that the same product was manufactured with both reactors. The main advantage of the continuous tubular reactor being that it could “handle” the heat output of a high solid content miniemulsion. Many more experiments have been run with this reactor, though their results are likely to be of limited use to the readers of this report. None the less, those results can be obtained by contacting the University of New Hampshire. On a similar note, a large amount of work has been done at UNH to develop a technique to monitor the miniemulsion polymerization process. Low Resolution Raman Spectroscopy (LRRS) was successfully applied as a monitoring technique. Again those results, though of scientific and industrial significance, are deemed of little use to the reader of this report. The LRRS monitoring of miniemulsion polymerization will be published in the scientific literature. Those results can be obtained by contacting the University of New Hampshire.

One of the results of this study is demonstration that miniemulsions of solid contents of industrial relevance¹² can be produced in a simple batch process by using a simple continuous tubular reactor. Consequently, it has been shown that not only is miniemulsion polymerization at high solid contents possible, but a continuous process can meet the requirements of industry. The combination of both high solid and continuous process is critical to make this technology attractive to industry and a potential solution to the needs of the DOT.

Summarizing, miniemulsion polymerization requires significant development, but has the potential to yield a paint with significantly shorter drying time compared to the current practice. Equally important, it should be possible to produce paints with additional attributes of great value to drivers operating at night and under adverse weather conditions.

Water precipitation

One approach might be to use super swelling polymers to “extract” the water to the surface of the film. Those super swelling polymers are commonly used in baby diapers. They are fairly expensive for a commodity polymer, around \$15/lb. However, their swelling properties are very good, and they can typically absorb 50 times their weight of salt water. The added cost per gallon of applied paint would be roughly \$0.50 / gallon, or a 10% price increase for a standard yellow WB acrylic paint. The difficult part of this technique would reside in the regular pulverization of a fine powder right behind the double spray nozzle of the “striper” trucks. It is difficult at this point to assess if the super-swelling polymer will wash away from the film’s surface, or will remain bonded. If it remains bonded, the traffic coating will never become of proper quality and will deteriorate rapidly. A final issue with super swelling polymer is the barrier it will offer to evaporation. Though the film will be created faster, a gel will remain at the surface of the film that may “splash” vehicles, as might the wet film.

In light of the drawbacks inherent in this technique, it does not seem sufficiently promising to warrant development efforts.

Destabilization

It is known that upon destabilization a waterborne coating will turn into a gel-like material. Furthermore it is known that such materials dry faster than stable formulations. For the purpose of a traffic paint, it is important to avoid any sort of destabilization before application to avoid plugging of the nozzle. After application it is possible to envision a spray of a polyvalent salt over the top of the wet coating to rapidly destabilize the dispersion. As illustrated in the section related to high solid content miniemulsion, addition of low amounts of salt can reduce viscosity, but excess of salt past that point can destabilize the emulsion as illustrated in figure 13. The use of polyvalent salt is significantly more effective at destabilizing emulsions than monovalent salts such as sodium chloride. It is necessary to raise the issue of the quality of the coating manufactured from such technique. It is known that salt will create ion channels when the film is dried. Such channels will allow water to reenter the film when it rains. These partially swollen films are likely to provide less wear resistance than conventional films. Most important is the ability of the film to retain and adhere to the retro reflective beads. Finally, to be effective the salt spray will have to be a solution of polyvalent salt in WATER. Though probably small in quantity that water will add to the overall amount of water that must be evaporated to form a finished film.

Because of the potential problems associated with this technique, only an experimental program will tell the DOT if this “trick” can be used to shorten the drying time.

Dry paints

This section addresses the concepts associated with dry paints. Industry has been using “dry paints” very successfully for over 20 years. The main application is the electrostatic deposition of a uniform layer of paint-powder, followed by high temperature annealing (curing). Thermoplastics are basically dry paints, their advantages are fairly well understood, and the main issue resides in the cost associated with its application. It is a slow process requiring large quantities of energy.

To make this type of paint more attractive it is necessary to find a faster and cooler application engineering solution. It is possible to use super critical carbon dioxide (SC CO₂) as a solvent for these dry paints. CO₂ acts as a plasticizer and allows annealing at lower temperatures. Unfortunately the triple point of SC CO₂ is at 78 bar and 32C, and although this is not particularly difficult to attain in a controlled environment, it implies that upon depressurization the CO₂ becomes a gas and absorbs a tremendous amount of energy, resulting in drastic cooling of the material it is in contact with. It would be interesting to study the possibility of designing a spraying apparatus that would maintain the supercritical state for a few seconds outside of the nozzle and absorb the evaporation energy. Though mostly theoretical at this point, such a technology would potentially revolutionize outdoor painting.

Potential for wear resistance improvements

Some very systematic studies of traffic paint wear resistance have been done by various states. Table 3 regroups the results of several of those studies. Clearly, waterborne coatings outperform alkyds and chloro rubbers. It is not so clear if the same waterborne coatings outperform urethanes and cold plastics.

	Arizona		Florida		Pennsylvania	
	OGAFC	PCC	DGAFC	OGAFC	DGAFC	PCC
Alkyd--White	163	>900	>900	101	341	390
Alkyd--Yellow	293	>900	>900	173	258	284
Chloro Rubber--White	478	>900	>900	255	444	470
Chloro Rubber--Yellow	159	>900	368	83	389	470
Water-base--White	>703	>900	>900	>900	505	823
Water-base--Yellow	>765	>900	>900	>900	474	684
Solv. Borne Epoxy--White	755	>900	>900	436	>1100	>1100
Solv. Borne Epoxy--Yellow	>900	>900	>900	400	>1100	>1100
Urethane--White	883	>900	>900	577	630	>1100
Urethane--Yellow	617	>900	>900	607	578	>1100
Thermoplastic--White	>900	>900	>900	824	>1100	413*
Thermoplastic--Yellow	>900	>900	>900	420	>1100	354*
Cold Plastic--White	>900	>900	>900	377	386	>1100
Cold Plastic--Yellow	>765	>900	>803	625	298	365
Foil Tape--White	>900	>900	>900	>900	NA	NA
Foil Tape--Yellow	>900	>900	>900	>836	NA	NA

Table 3. Estimated service life by class (median lifetimes in days)¹³

NA - Not Available, OGAFC - Open-graded asphaltic concrete, * - Data may not be reliable due to snowplow damage, DGAFC - Dense-graded asphaltic concrete, PCC - Portland cement concrete

Most importantly, none of these studies were done in a northern state where the weather requirements are as severe as in New Hampshire. It would be particularly useful to validate a paint system under the severe damage inflicted by snowplows and abrasion from cars driving over salt and sand. A test site (deck trials) in the northern part of NH, on a high traffic road such as 93 between Concord and Plymouth would be very well suited. Most likely, useful conclusions could be drawn after a single winter. Over the same section of highway, strips of 5 different systems could be painted. These systems should include waterborne regular and fast dry, polyurethane, epoxy and thermoplastics.

In the following section we intend to review two possibilities to improve the durability of waterborne binders. Both options address issues related to the improvement of the polymeric binder. Table 4 provides a simple estimation of their merits. The option of introducing crosslinking units in the binder is highly attractive since it offers high benefits for a low cost. Both technical options can be implemented separately or in combination.

<i>Potential solution</i>	<i>Benefits</i>	<i>Risk / difficulty</i>	<i>Added cost to product</i>
Insertion of crosslinker	High	Medium	Low
Hybrids PU/Acrylics	High	Medium	Medium

Table 4. Risk/Benefits analysis of wear resistance improvements of traffic paint binders.

In order to understand the potential improvements of traffic paints it is very useful to learn from the well studied properties of tires. Tires and traffic paints need to provide similar properties of flexibility and abrasion resistance over a wide range of temperature. The standard laboratory test for wear resistance is called the "Mar resistance test". This

test is done by rubbing a solvent under a fixed load (pressure) onto the tested material. Those tests have shown that the wear resistance can be improved by modifying the following characteristic of the binder:

- Lowering the glass transition temperature
- Reducing the distribution width of the glass transition temperature
- Increasing the crosslinking density
- Increasing the molecular weight

Insertion of crosslinker

Immediately after UNH approached the NH-DOT in early 1998, Rohm & Haas, one the largest producers of traffic paint (binder) in the United States, started to commercialize a new product, called Rhoplex fastrack® HD-21. This product includes a crosslinking system, although the company is not willing to disclose the technical nature of this crosslinking system. Test results show clearly that this latest traffic paint binder improves wear resistance very significantly.

A crosslinker system is a chemical function, A, that condenses or reacts with another chemical function, B. Upon reaction they connect existing polymeric chains. In a waterborne system they allow the interconnection of unit cells (figure 1 - Polymer binder, swollen with solvent and coalescing agents) and provide a significantly higher cohesion to the newly formed matrix. Figure 16 symbolically illustrates this effect.

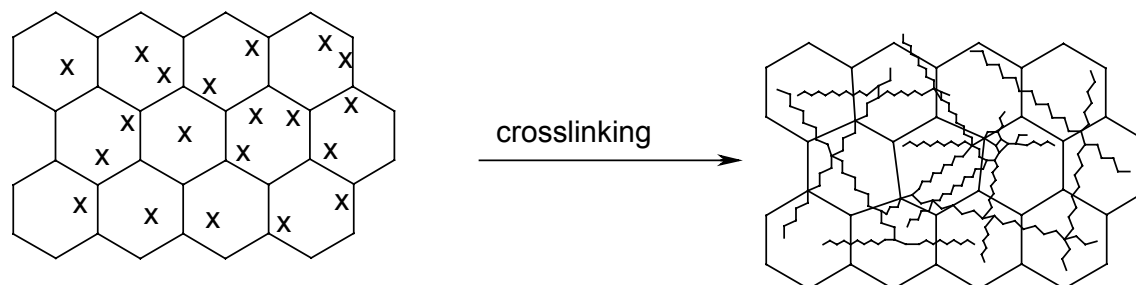


Figure 16. Symbolic representation of the crosslinking effect.

The direct impact of crosslinking is to increase the crosslinking density and to increase the molecular weight of the polymer. Both of these effects are known to improve wear resistance. The indirect benefit of crosslinking is the possibility of lowering the glass transition temperature. In a simplistic approach, the minimum film formation temperature (MFFT), or temperature at which a paint film can be applied, is closely related to the glass transition temperature. The MFFT needs to be lower than the application temperature, usually around 5C for traffic paints. The lower the MFFT, the easier it is to create a film. Unfortunately, with a lower MFFT a lower glass transition is necessary, and a more tacky (adhesive) binder is made. Crosslinking is a good remedy to this issue since it allows the use of a lower glass transition while eliminating the tacky properties. A comparative example can be made with a tire made of a crosslinked rubber (very low glass transition, highly crosslinked with sulfur) and rubber glue (same low glass

transition, without crosslinks). The tire is indeed not tacky or adhesive, while the rubber glue is very tacky and adhesive. Both remain very elastic.

One of the documented drawbacks of crosslinking is lower retro-reflective bead retention. This is the direct consequence of the lower tackiness. Fortunately bead retention can be improved by modifying the surface of the beads with a chemical that will react (condense) with the crosslinker, and hence chemically attach the beads to the binder. Beads are already surface modified, generally with a silane to provide compatibility between the binder and the bead surface. Here we suggest going one step further by “attaching” the beads to the binder.

Crosslinking in waterborne paints can be done several ways. A majority of the solutions involve the mixing of two different products (2-pack) immediately before application. Though extremely efficient these systems imply the use of two holding tanks, two feeding lines and a different type of spray nozzle. Some of the more recent crosslinking systems combine both types of functions in one system (1 pack). With these systems two types of polymer binder particles are used, each containing a different type of function that upon film formation (coalescence) react together to create the crosslink. The 1-pack systems are not as stable over time, and have shorter storage life.

Finally, the most attractive family of crosslinking system is named radiation curable coatings. Typically radiation (ultra violet light – UV light or electron beam - EB) activates a free radical initiator, and the crosslinking reaction occurs through free radical polymerization. The use of UV is most attractive for outdoor coatings, since UV light is readily available from the sun. Because of the relative opacity of the films, only the surface layer of the traffic paint would be irradiated and crosslinked. This does not present a significant issue, since only the surface of the film needs to present wear resistance properties. As the film degrades mechanically, a new layer is exposed to the sunlight and consequently crosslinks. After a few days / weeks, we would have a high quality wear resistant coating.

A simple waterborne UV curable coating might include

1. An oligomeric acrylate or acrylate polyurethane
2. A mixture of monofunctional acrylate (or methacrylate)
3. A photoinitiator package

The better waterborne UV curable coatings for traffic paint applications would involve polyurethane binders in combination with acrylate units. Not only are they tack-free before curing, they can offer mechanical properties sufficient for initial wear resistance associated with “drive over”.

Although significant development challenges remain, this approach to improved wear resistance seems highly promising.

Hybrid Acrylic Polyurethane

Binder synthesis

Durability and wear resistance can be overcome by changing the molecular characteristics of the binder.

In this section we consider developing a different type of polymer binder by creating a hybrid of Polyurethane (PU) and Polyacrylates to produce a paint with high wear and high water resistance at a competitive cost. Polyurethanes are a very broad family of polymers. Their chemistry is very flexible and their structure can be tailored to fit the requirements of a very large range of applications. They are encountered in everybody's life from the rubber soles of shoes and the foam in couches and mattresses, to hardwood floor finishes. They are typically the product of the addition of diol and a diisocyanate. The diol molecule is typically a flexible polyether, with variation in the flexibility, while the diisocyanate is a "hard" segment. The urethane bond resulting from the condensation of an alcohol onto an isocyanate is chemically very stable. The combination and the rearrangement of the flexible and hard segment into micro domains are at the origin of the wear resistance properties of polyurethanes. Polyurethanes are expensive, roughly 2 to 3 times the cost of acrylates, and are rarely used as the sole binder. By properly combining a polyurethane and a polyacrylate as shown in figure 17, it is possible to minimize the amount of polyurethane used while maintaining the improved wear resistance properties.

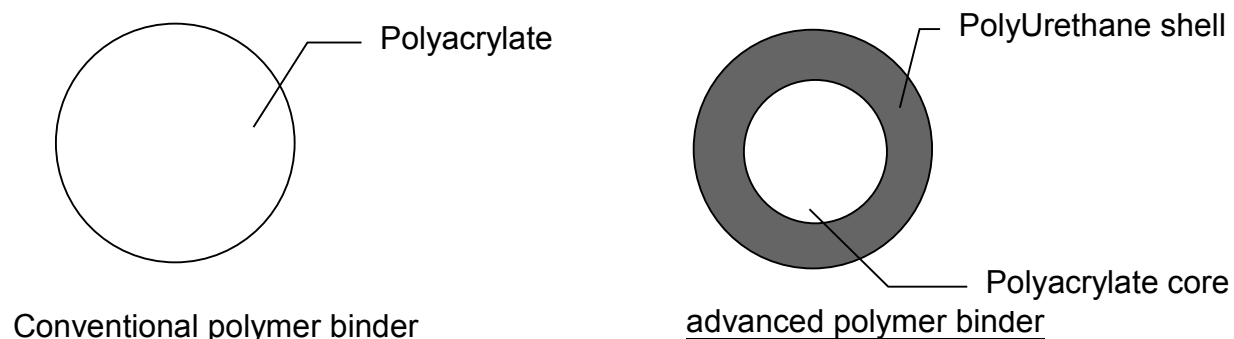


Figure 17. Comparative structure of a conventional and hybrid polymer binder.

The polyurethane shell provides abrasion resistance and a higher cohesion of the paint, while the polyacrylate core provides weather resistance, durability, and a lower cost.

The isocyanate chemical function is very reactive with water. Consequently it is not possible to prepare polyurethanes in the presence of a water phase. To make a polyurethane dispersion (PUD) the following technique has to be used.

In a first step a prepolymer containing one carboxylic acid function and two isocyanate groups is prepared in an organic solvent. In the second step the prepolymer is neutralized with a tertiary amine, and mechanically dispersed into water, usually through a phase inversion technique. Then a di-primary amine is added to the dispersion and the isocyanate condenses very rapidly with the amine, creating a urea bond. Typically, particles of 100-300nm are obtained, with polymers having a molecular weight in the 100,000g/mole range. Though these polymers are technically made of both polyurea and polyurethane, they are commonly referred as polyurethanes.

This technology has been modified to allow the preparation of polyurethane/acrylic hybrid dispersions. In this modification, a mixture of acrylate monomers replaces the organic solvent of the first step. After chain extension a water-soluble initiator is added

to allow the free radical polymerization of the acrylate(s). Depending on the particular composition of the acrylate solution and the functionality of the polyurethane, upon phase separation a semi interpenetrated or interpenetrated network is obtained. In all cases, the properties of the resulting hybrid films exceed the properties of an equivalent film obtained by blending a PUD and acrylic latex.

One of the drawbacks of the PUD prepared by such technique is the high level of hydrophilic functionality resulting from the presence of the neutralized carboxylic groups. Such groups produce poor resistance to polar solvents such as methanol (used in windshield wiper fluid) in films prepared from PUD (hybrids or not).

It is possible to combine the polyurethane acrylate hybrid technology with recent developments in miniemulsion polymerization. The preparation of the advanced polymer binder would involve 4 steps:

1. A mixture of acrylate monomers (EHMA, BA, 2Hydroxy-ethyl-methacrylate) is generated
2. The previous mixture is used as a solvent to synthesize the polyurethane through classic di-isocyanate + diol addition (for example polymeric MDI or TDI + low molecular weight diol).
3. The PU / acrylate solution is mini emulsified with a sonicator (ultrasound apparatus), in presence of water and emulsifier.
4. The dispersion is polymerized through addition of a thermal initiator. The process is tuned to provide low glass transition temperature, high molecular weight and narrow glass transitions.

It seems likely that use of such an advanced polymer binder would dramatically improve the performance of traffic paint. The insertion of a UV crosslinker in the binder is perfectly compatible with the use of a new hybrid PU/Acrylate binder. Therefore, these two innovations should be combined if possible in order to produce a paint with significantly improved wear resistance.

Performance cost analysis

To gain insight into whether the concept of hybrid paint is realistic from a commercial perspective, an effort was made to project the cost of such a product. Table 5 regroups the essential numbers necessary to compare two paint systems.

Traditional emphasis on cost per gallon or cost per linear foot excludes all consideration of how long the paint once applied remains sufficiently bright to serve its intended purpose. Indeed, using cost per gallon excludes even the cost of application. While this was the logical result of composition-based procurement, it provides no incentive to produce paint that does a better job of remaining in place and staying bright enough to serve its intended purpose. Performance based analysis seems essential.

In analyzing these numbers, therefore, this table evaluates cost in terms of the useful life of the paint once applied onto a road or highway. This is described as the effective applied price, in \$/foot/year.

<i>Technology</i>	<i>Traffic Paint</i>	<i>White</i>	<i>Yellow</i>
100% Acrylic	Formulated paint Price (\$/gal.)	4.5-4.75	5.25-5.5
	Amount of wet binder (lb./gal.)	4.8	4.8
	Dry acrylics cost (\$/lb)	2	2
	Applied price (\$/foot)	0.04	0.05
	Expected life (year)	1	1
	Effective Applied price (\$/foot/year)	0.04	0.05
Hybrid PU/Acrylic	Formulated paint projected price (\$/gal)	~5.5	~6.5
	Price increase (%)	22	18
	Amount of binder (lb./gal.)	4.8	4.8
	Dry PU/Acrylics cost (\$/lb)	3	3
	Applied price (\$/foot)	0.06	0.07
	Expected life (year)	2	2
	Effective Applied price (\$/foot/year)	0.03	0.035

Table 5. Comparative cost analysis of hybrid PU/acrylic paints.

Table 5 shows clearly that an effective applied price advantage of 25% to 30% seems likely with the advanced PU/acrylate hybrid binder. Please note that this table almost certainly underestimates the economic benefits from better paints since it assigns no value to the improved safety that comes from having roads with lines capable of “surviving” a winter in New Hampshire.

Application cost analysis for the NH-DOT.

On 10.22.98, the writer of this report took a “road-trip” with a “striper” crew from the NH-DOT Traffic bureau. Information regarding the equipment onboard a “striper” was obtained.

Variable cost:

On that day 36000 feet of traffic paint was applied. On a better day 100,000 feet are applied.

The combined variable labor cost for that day was about \$600.

The variable cost of labor for application varies from 1.6 cents/foot to 0.6cents/foot.

The variable cost of the paint is 3 to 4cents/foot (depending on paint grade)

The variable cost of gas is 0.01 cents/foot (negligible)

Equipment depreciation cost of a “striper” truck that costs \$70,000 and last 300,000 miles, is 0.05 cents/foot (negligible).

Total cost to NH-DOT = 3.6 to 5.7 cents/foot.

This cost compares favorably to the standard contractor price of 8 cents/foot (applied).

It is important to note that material costs are 2 to 5 times higher than labor, and that equipment costs are negligible.

Potential for bead retention improvements.

Beads are typically made of glass and are surface modified with silanes to become non-polar and hence “compatible” with traffic paints. The interaction between coating and beads is minimal and limited to adhesions. Because of strong surface shear caused by traffic, beads are sheared off the coating rapidly, generally within a few months. Winter conditions and rapid change of temperature is even more stressful on the bead-coating

“association” since they have very different thermal expansion coefficients. An alternative to glass beads is impact-modified polycarbonate or impact modified polymethylmethacrylate (PMMA) beads. Either can be made spherical if necessary and strong enough to withstand the compression shocks of road traffic. Those beads can also incorporate organic dyes, such as color, UV, and temperature sensitive or humidity sensitive dyes. Any of those dyes would provide the type of safety improvement expected from a new generation of traffic paint. Beads based on polymers have thermal expansion coefficient practically equal to the one for traffic paints. Consequently no bead loss would come from thermal expansion coefficient disparities. Finally the surface of the beads can be tailored to “react” with the crosslinking system of a new traffic paint to create very strong chemical bonds between beads and coating. Such beads would not be sheared off the coating, but would wear only through surface abrasion. Possibly structured beads could be designed to have internal reflectors and conserve retro-reflective properties even when they are flush with the traffic paint surface.

Conclusions and Recommendations

Drying time. After reviewing a range of possible ways to improve the drying time of paints after application to the road surface, two approaches were identified that seem worthy of further exploration:

- Development of a spray to destabilize the paint. An experimental program would be required to develop, test, and refine this technique. The best way to proceed would be with a limited phase I effort to provide "hands-on" information with which to evaluate its potential.
- Development of dry-air “train”. This is likely to be useful primarily for high-use highway situations. It represents an improved version of the present practice of having a large number of Transportation Department vehicles follow behind the paint striper to keep vehicles from crossing the line before it dries.
- An improved waterborne paint produced through miniemulsion. This has the potential for being faster drying, and also to have additional useful properties. Significant development challenges would have to be overcome in order to utilize this relatively new technology. The polyurethane/acrylate hybrid option described below would have many of the same properties as well as improved wear resistance. Therefore, while miniemulsion technology development should be carefully monitored, priority probably should be given to developing the polyurethane/acrylate hybrid option.

Wear resistance. After careful review of all known existing technologies, one new approach was identified that seems to offer potential for significantly improved yet cost-effective lines for New Hampshire's roads and highways.

- Development of a polyurethane/acrylate hybrid system with UV-light induced crosslinking prepared by miniemulsion polymerization. The polyurethane shell provides abrasion resistance and a higher cohesion of the paint, while the polyacrylate core provides weather resistance, durability, and a lower cost. Combined with recent development of crosslinking systems using chemical reaction to obtain a significantly higher cohesion, the result should be a paint that

is cost competitive yet capable of staying bright and reflective for a significantly longer period of time.

- Develop better retro-reflective coatings through the use of alternative materials. While technically not part of the improved paint, sustained reflectivity requires that the glass beads now used be replaced with a slightly improved version to enhance retention when subjected to snow plows and abrasion from sand and salt. The bead and paint need to be an integrated system.

Testing and evaluation. Published research data evaluating alternative coating options all comes from relatively warm weather states. It is in the long-term interest of the NH-DOT and other northern states to develop a test-deck for evaluation of alternative paints when subjected to the serious wear and tear that results from keeping roads clear in winter. This is needed to properly evaluate present paints as well as for new candidates. Therefore, it is recommended that New Hampshire establish such a test deck at a location of high use in the north-central part of the state, perhaps on I-93 between Concord and Plymouth, or between Concord and Manchester.

Procurement specifications. Finally, the evaluation criteria for paints purchased for use on New Hampshire roads and highways should be carefully reviewed and rewritten so that they are performance based. Current absence of a minimum level of binder was identified as having potential to significantly impact paint quality. This change would be immediately useful in ensuring that paints currently available are evaluated in terms of their cost effectiveness. Equally important, this change is an essential precondition to the development of new paints that have the longer useful life required by drivers using New Hampshire roads and highways.

Resources for a center to develop alternative technologies

Realistically, development of significantly improved paints is a major undertaking that requires resources beyond those reasonably available from a single state. Therefore, a course of action is identified that suggests a limited initial program while resources are being identified for the longer term effort.

Phase I -- Initial Steps.

The initial effort should focus on development of a test deck in central New Hampshire at which paint alternatives could be systematically evaluated in a standardized environment. While this need not be expensive, it should be used to produce publishable performance data. A collaborative effort with University researchers might be optimal since it would yield data generated by an independent third party.

At the same time, present procurement regulations should be carefully reviewed. A practical approach might be to develop -- or adopt from somewhere else -- one or more alternative standards as the basis for a limited procurement for application over one or two years, as well as at the test deck. Operational experience with the paints procured and applied through this process could be evaluated, perhaps by an independent third party. Again, this might be a useful role for university researchers.

These steps might be supplemented with limited experimentation with one or more of the recommended options, if funds are available. It is hard to overstate the benefits from a limited research effort even as a larger program is being designed, since the practical experience greatly improves the knowledge base for the larger program.

For example, an application engineer employed by the University and working in cooperation with the traffic bureau would manage the test deck, and be able to provide careful scientific comparison of various existing commercial paints. That person would also focus on developing an accelerated lab test to provide faster performance information. Such collaboration between UNH and the DOT would provide the DOT with the ability to select traffic paints on the basis of price-performance, instead of formulation and cost. The financial support required for such a project is about \$150,000 per year, exclusive of related costs for the traffic bureau.

Phase II -- developing significantly better paints.

To be most effective, a proper traffic paint development team needs to be constituted of three sub groups.

The first is an application-engineering group. It would work closely with “striping” crews, and work on the engineering constraints associated with any new technology. For example, such a group would implement the installation of a test deck, in collaboration with the traffic bureau. They would oversee the rigor of field tests and collect the results. This same group would study the development of new types of spray guns, or the design of a drying train. In practice, this group serves as the primary interface with the Transportation Department, and shares with it focus on making systems work under realistic operating conditions.

The second is a formulation group. It would focus on the additives combined with the polymeric binder to manufacture a ready-to-apply paint system. This group would provide rheological solutions to the requirements of the application group. It would oversee film formation properties, and test the properties of the finished coating, such as measuring the wear resistance properties and the effectiveness of the UV crosslinking system.

The third is a polymer-engineering group. This last group must be capable of designing a wide variety of waterborne polymeric binders. They can control both the chemical architecture of complex binders as well as the microstructure (also called morphology) of the dispersed system. They are to insure that the technology used can be scaled-up and that the various chemicals employed are of commercial reality. They would interface directly with the formulation group.

Such a traffic paint development center needs to have these three groups staffed with experienced professionals. They need to be assisted by more additional junior personnel. Upon creation of such a center of excellence a minimum of 6 persons would have to be hired. The expected time necessary to develop some effectively implemented results is likely to be 2 to 3 years. The focus of the center is likely to shift over time from the current issues discussed at length in this report to more universal

issues related to the traffic coatings required for improved traffic safety, such as environmental responsiveness (e.g., temperature, humidity, sun) to provide drivers with necessary information (e.g., black ice, potential hydro-planning).

A crude estimation of the cost of such a center for its first 3 years is about 2.5 million dollars. This seems reasonable in the context of the fact that some \$300,000,000 is spent annually in the United States on the purchase of traffic paint, and that all drivers depend on clear lines to drive safely.

			Year 1	Year 2	Year 3	Total
A. Faculty		Base				
	PI	0				
		Acad	180,000	189,000	198,450	567,450
		Summer	40,000	42,000	44,100	126,100
Total Faculty			220,000	231,000	242,550	693,550
B. Other Personnel						
	Pat Staff		90,000	94,500	99,225	283,725
Total Salaries & Wages (A+B)			310,000	325,500	341,775	977,275
C. Fringe Benefits			3,360	3,528	3,704	10,592
			97,200	102,060	107,163	306,423
		Subtotal	100,560	105,588	110,867	317,015
Total Salaries, Wages & FB (A+B+C)			410,560	431,088	452,642	1,294,290
D. Tuition			0	0	0	0
E. Equipment			100,000	100,000	100,000	300,000
F. Travel			20,000	21,000	22,050	63,050
G. Other Direct Costs						
Materials & Supplies			50,000	52,500	55,125	157,625
		Total Direct Costs	580,560	604,588	629,817	1,814,965
		MTDC Base	480,559	504,589	529,816	1,514,964
H. Facilities & Administrative			211,446	222,019	233,119	666,585
		Total Direct + F&A	792,006	826,607	862,936	2,481,549
I. Cost Sharing (if any)			0	0	0	0
J. Program Income (if any)			0	0	0	0
		Total Project Costs	792,006	826,607	862,936	2,481,549

F&A Rate	44.00%	44.00%	44.00%
Full Fringe Rate	36.00%	36.00%	36.00%
FICA Rate	8.40%	8.40%	8.40%
Inflation Factor	105.00%	105.00%	105.00%

Appendix

Modeling of the heat transfer.

The generalized heat equation¹⁴ was used to establish the models.

$\rho \equiv$ Density

$C_p \equiv$ Specific Heat

$k \equiv$ Thermal conductivity

$$\rho C_p \left(\frac{\partial T}{\partial t} + v \nabla T \right) = k \nabla^2 T + q' \quad q' \equiv \text{Rate of heat generation}$$

$T \equiv$ Temperature

$t \equiv$ Time

$v \equiv$ Velocity

$\nabla \equiv$ Del operator

Equation 1

Since there is no velocity associated with the problem at hand, that term drops out of the equation. The one dimensional heat equation without the velocity term is the following:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} + \Psi \quad \alpha = \text{Thermal Diffusivity} = \frac{k}{\rho C_p}$$

$$\Psi = \frac{q'}{\rho C_p}$$

Equation 2

The above equation can be non-dimensionalized before it is solved. This was accomplished by introducing the following non-dimensional variables:

$$\Theta = \frac{T - T_s}{T_o - T_s} \quad \Theta = \text{Dimensionless Temperature}$$

$$T_o = \text{Initial Temperature}$$

$$T_s = \text{Temperature of Surrounding}$$

$$s = \frac{t}{t_{scal}} \quad s = \text{Dimensionless time}$$

$$t_{scal} = \text{Max time}$$

$$\eta = \frac{x}{L} \quad \eta = \text{dimensionless distance}$$

$$L = \text{Max length}$$

Due to the change of variables, equation two became:

$$\frac{\partial \Theta}{\partial s} = \frac{\alpha t_{scal}}{L^2} \frac{\partial^2 \Theta}{\partial \eta^2} + \frac{q' \cdot t_{scal}}{\rho C_p \cdot (T_o - T_s)}$$

Equation 3

Equation three was solved by numerical approximation. The program written to solve equation three converted back to dimensional variables when it printed the solution at the different time steps.

The computer program made use of the Crank-Nicolson algorithm. Crank-Nicolson was chosen for several reasons. This algorithm more closely approximates the actual solution than other algorithms. The following equation is the Crank-Nicolson approximation of equation three:

$$\frac{\Theta_j^{n+1} - \Theta_j^n}{\Delta s} = \frac{\alpha t_{scal}}{2(\Delta \eta)^2 \cdot L^2} \cdot \left((\Theta_{j+1}^n - 2\Theta_j^n + \Theta_{j-1}^n) + (\Theta_{j+1}^{n+1} - 2\Theta_j^{n+1} + \Theta_{j-1}^{n+1}) \right) + \frac{q' \cdot t_{scal}}{\rho \cdot Cp \cdot (T_o - T_s)}$$

Equation 4

“n” represents a time step and “j” is a step in the one dimensional space. The one dimensional space η is divided in a total of k steps. This equation can be rearranged by solving for Θ^{n+1} in the following manner:

$$\Theta_j^{n+1} - \Theta_j^n = \frac{\Delta s \cdot \alpha \cdot t_{scal}}{2 \cdot (\Delta \eta)^2 \cdot L^2} \cdot \left((\Theta_{j+1}^n - 2\Theta_j^n + \Theta_{j-1}^n) + (\Theta_{j+1}^{n+1} - 2\Theta_j^{n+1} + \Theta_{j-1}^{n+1}) \right) + \frac{\Delta s \cdot q' \cdot t_{scal}}{\rho \cdot Cp \cdot (T_o - T_s)}$$

Equation 5

Defining the following as constants:

$$A = \frac{\Delta s \cdot \alpha \cdot t_{scal}}{2 \cdot (\Delta \eta)^2 \cdot L^2} \quad B = \frac{\Delta s \cdot q' \cdot t_{scal}}{\rho \cdot Cp \cdot (T_o - T_s)}$$

Equation 5 becomes:

$$\Theta_j^{n+1} - \Theta_j^n = A \cdot \left((\Theta_{j+1}^n - 2\Theta_j^n + \Theta_{j-1}^n) + (\Theta_{j+1}^{n+1} - 2\Theta_j^{n+1} + \Theta_{j-1}^{n+1}) \right) + B$$

Equation 6

Moving all Θ^{n+1} to the left side of the equation produces the following:

$$\Theta_j^{n+1} - A \cdot (\Theta_{j+1}^{n+1} - 2\Theta_j^{n+1} + \Theta_{j-1}^{n+1}) = \Theta_j^n + A \cdot (\Theta_{j+1}^n - 2\Theta_j^n + \Theta_{j-1}^n) + B$$

Equation 7

$$-A \cdot \Theta_{j-1}^{n+1} + (2 \cdot A + 1) \cdot \Theta_j^{n+1} - A \cdot \Theta_{j+1}^{n+1} = \Theta_j^n + A \cdot (\Theta_{j+1}^n - 2\Theta_j^n + \Theta_{j-1}^n) + B$$

Equation 8

Dividing equation 8 by a negative A produces the following:

$$\Theta_{j-1}^{n+1} + \left(-2 - \frac{1}{A} \right) \cdot \Theta_j^{n+1} + \Theta_{j+1}^{n+1} = \frac{-1}{A} \cdot \Theta_j^n - A \cdot (\Theta_{j+1}^n - 2\Theta_j^n + \Theta_{j-1}^n) - \frac{B}{A}$$

Equation 9

The equation above produces a tridiagonal system of equations. The left side of the equation produces the solution matrix $[\Theta_j^{n+1}]$, the right side of the equation is the forcing


```

for(i=0;i<NUM;i++){ // initializes U at time zero
    soln[i][0]=(float)x;
    U[i]=0.;
    phi[i]=0.;
    a[i]=1.;
    b[i]=(float)gamma;
    c[i]=1.;
    x+=dn;
}
U[0]=1.; U[1]=1.; U[2]=1.; c[0]=2.;
for(i=0;i<NUM;i++)
    soln[i][1]=U[i];
KNT=0;
j=2;
for(s=0;s<=1.;s+=ds){
    PHIFIX(phi,U,gamma,rho);
    tridag(a-1,b-1,c-1,phi-1,U-1,NUM);
    for(i=0;i<NUM;i++)
        soln[i][j]=U[i];
    time[j-2]=s*tscal;
    j++;
}
fprintf(outfile,"x      Time 0.      ");
for(j=0;j<COL-2;j++)
    fprintf(outfile,"Time %.2f      ",time[j]);
fprintf(outfile,"\n");
for(i=0;i<NUM;i++){
    for(j=1;j<COL;j++){
        soln[i][j]=((float)To-(float)Tg)*soln[i][j]+(float)Tg;
    }
    for(j=0;j<COL;j++){
        fprintf(outfile,"%f      ",soln[i][j]);
    }
    fprintf(outfile,"\n");
}
fclose(outfile); // closes the file HEAT
}

void PHIFIX(float phi[], float U[], double gamma, double rho){
    int i;
    for(i=1;i<NUM-1;i++) // solves for phi
        phi[i]=((4+(float)gamma)*U[i])-U[i-1]-U[i+1]+(float)rho;
    phi[0]=((4+(float)gamma)*U[0])-(2*U[1])+(float)rho;
    phi[NUM-1]=((4+(float)gamma)*U[NUM-1])-(U[NUM-2])+(float)rho;
}
#define NRANSI
#include "nrutil.h"

void tridag(float a[], float b[], float c[], float r[], float u[],
    unsigned long n)
{
    unsigned long j;
    float bet,*gam;

    gam=vector(1,n);
    if (b[1] == 0.0) nrerror("Error 1 in tridag");
    u[1]=r[1]/(bet=b[1]);
    for (j=2;j<=n;j++) {
        gam[j]=c[j-1]/bet;
        bet=b[j]-a[j]*gam[j];
    }
}

```

```

        if (bet == 0.0)  nrerror("Error 2 in tridag");
        u[j]=(r[j]-a[j]*u[j-1])/bet;
    }
    for (j=(n-1);j>=1;j--)
        u[j] -= gam[j+1]*u[j+1];
    free_vector(gam,1,n);
}
#endif NRANSI

```

Experimental conditions for miniemulsion polymerization

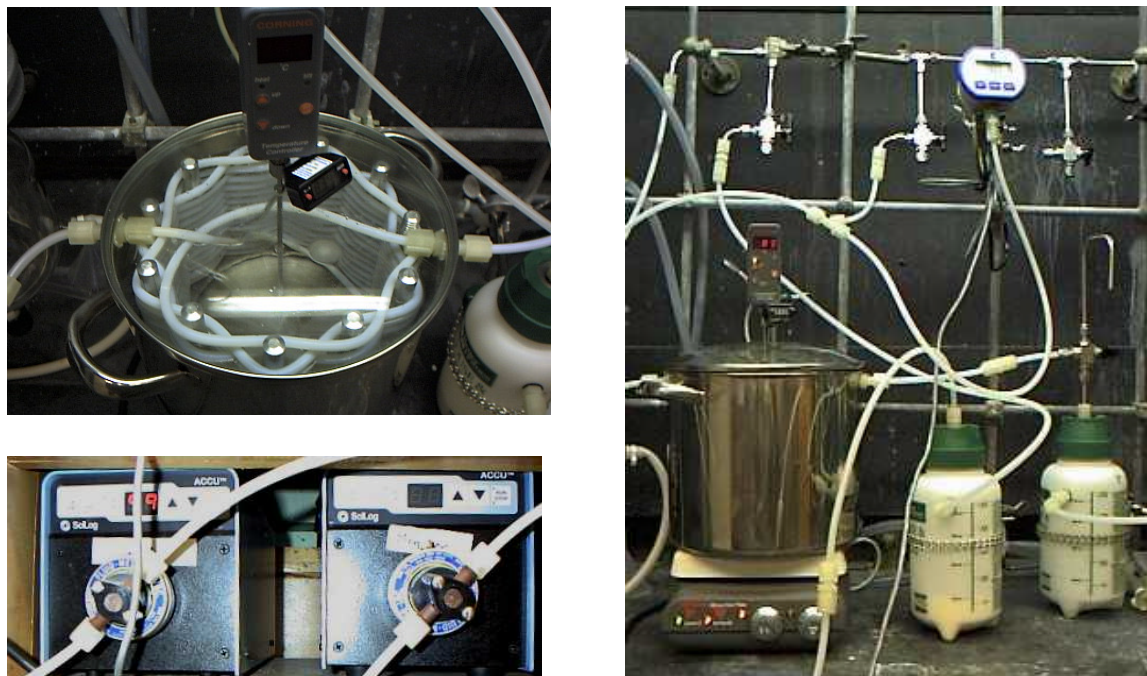
Date	11/12/98
Monomer	Styrene
Process	Batch mini emulsion
Reactor type	250 mL
Reaction temperature (°C)	70
Solid Content (theoretical)	61.7%
Solid Content (experimental)	56.1%
Size	139nm
pH	8.96
Polymerization time	120 minutes
Samples	Odd times

Table A1. Process conditions and results for the miniemulsion polymerization of styrene in batch with a monomer content of 65% reduced to 62% by addition of water and salt.

<i>Compound</i>	<i>Part per hundred part monomer</i>
Sodium Dodecyl Sulfate	2
di-Ethylhexyl sulfosuccinate	2
Hexadecane	3
Divinylbenzene	2
NaHCO₃	0.2
Sodium persulfate	0.2
UV Dye	0.06

Table A2. Recipe for the batch minimemulsion of styrene.

Experimental conditions for continuous miniemulsion polymerization



Picture A1. Experimental continuous tubular reactor at the University of New Hampshire. Top left: the white Teflon tube is the tubular reactor. Bottom left: reciprocating displacement pumps ensuring circulation in the reactor. Right: reactor, with feeding tanks, collecting tank and pressure lines.

Experiment #	TRM 024C	TRM 024B
Date	1/24/99	1/22/99
Monomer	Styrene	Styrene
Process	Continuous	Batch
Reactor type	Tubular	250 mL
Reaction Temperature (°C)	70	70
Solid Content	37.3%	40.5%
Diameter	118nm	118nm
Conversion	95%	100%
Polymerization time	90 min.	90 min.
Sampling rate		Every 10 min.

Table A3. Comparative process conditions and results for the miniemulsion polymerization of styrene in batch and in continuous.

Compound	Part per hundred part monomer
Sodium Dodecyl Sulfate	2
di-Ethylhexyl sulfosuccinate	2
Hexadecane	3
Divinylbenzene	2
NaHCO₃	0.2
Sodium persulfate	0.2

Table A4. Recipe for the batch and continuous minimemulsion of styrene.

-
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