

EFFECT OF HEAT HISTORY DURING MANUFACTURE ON SBS MODIFIED BITUMEN COATING QUALITY

DC. PORTFOLIO and F.A. FENSEL

Tremco, Inc.
Cleveland, Ohio

Manufacturers of styrene-butadiene-styrene (SBS) block copolymers used to produce modified bituminous membranes have documented that certain conditions of temperature and time should be avoided during the process of blending SBS polymers with the bitumen. In the manufacture of polymer modified asphalt blends, the proper time, temperature and mixing are necessary to incorporate the polymer into the asphalt. Excess time and temperature can result in significant thermal degradation of the polymer with resultant impact on both the physical and performance properties of the coating.

The manufacturing information available is somewhat dated and may not involve production equipment currently in use in the United States. As a result, a study was initiated to determine the manufacturing parameters under which coating properties would be optimum at the appropriate polymer loading.

The properties used to characterize modified coating physical properties included softening point, penetration, flexibility failure temperature, viscosity and modulus. The extent of polymer degradation in the coating was determined through gel permeation chromatography and subsequent analysis of the molecular weight distributions of the polymer. The weatherometer was used to determine the predicted performance of the coating.

KEYWORDS

Asphalt, bitumen, modified bitumen, polymer/asphalt blends, styrene-butadiene-styrene (SBS), thermal degradation.

INTRODUCTION

Styrene-butadiene-styrene block (SBS) copolymers were introduced as modifiers to improve the properties of bitumen in the early 1970s.¹ Since that time, a significant amount of research has been completed both on a laboratory scale and in some specific larger scale equipment. To date, however, this information has not been compiled to determine the effect of the total mixing process used in the preparation of SBS modified coating from which the membrane is produced. The effect of one specific process and a set of predetermined parameters on the quality of the coating, as measured by commonly accepted physical tests as well as gel permeation chromatography, was determined in a group of controlled plant experiments.

The study was initially undertaken to optimize the manufacturing process both in terms of quality of the SBS modified coating and plant operational efficiency. This was necessary since the plant was not in continuous operation at various times during the year. Also, the idea of holding

prepared coating batches for extended periods was proposed as a way to improve operating efficiency.

A search for information from polymer suppliers including literature and patents was undertaken. Little information related to coating production on the macro scale was found. It was well-known, based on laboratory scale experiments, that the SBS polymers used in SBS modified membranes were susceptible to thermal degradation. The critical temperatures were documented,² however, the effect of thermal history on a plant scale was not well documented.

Gel permeation chromatography (GPC) was selected as the method of choice to determine the condition of the polymer in terms of thermal degradation. This method separates the polymer from the asphalt, and through comparison with untreated polymer and polystyrene standards gives an indication of degradation of the polymer. A survey of commercially available SBS modified membrane products indicated that the level of degradation of the SBS polymer in the coating varied widely from virtually no degradation to severely degraded.

A survey of the equipment used to manufacture SBS coating revealed that both equipment and process varied significantly. Low speed mixers can require up to 10 hours to complete the blend of polymer with asphalt. High speed, high shear mixers complete the asphalt/polymer blend in less than two hours at the same temperature. No attempt was made to relate specific process to the degree of thermal degradation of the polymer.

While thermal degradation was selected as the focus of this work, it is not the only factor which contributes to the quality of an SBS/asphalt modified coating. The formulation of the coating, particularly the choice of a polymer compatible asphalt, is the foundation for any work concerned with processing. A poorly formulated coating cannot be made better through processing. However, a well-formulated coating can be adversely affected during production if the process results in thermal degradation of the polymer. The specific type of SBS polymer used impacts the resultant physical properties of the blend with asphalt. A linear SBS polymer was used with an asphalt which resulted in a high degree of compatibility with the polymer. The use of antioxidant materials to reduce thermal degradation due to heat history during manufacture was not considered for this particular group of experiments.

In a survey of polymer manufacturers' literature,³ four parameters were found that controlled the speed of blend process for SBS and asphalt:

- Polymer particle size. Powdered polymer, while more expensive, blends faster than the crumb form.

- Temperature and heat transfer rate of the process. The higher the temperature and heat transfer rate, the faster the blend can be completed. Excessive temperatures, however, result in significant thermal degradation of the polymer especially if coupled with long processing times.
- Mechanical shear energy input to the blend after the polymer particles have become small enough to be mobile in the blend. High shear rates result in faster completion of the blend than low shear rates.
- Polymer type. Radial polymer is more effective in improving asphalt properties than linear at equivalent loadings. However, it is more difficult to blend with asphalt than the linear grade.

As is evident, there are conflicting opportunities to improve the manufacturing efficiency. High temperatures which can speed the blend process can also lead to thermal degradation. In the worst case, the SBS/asphalt blend can gel into a solid mass within the mixer. In a more moderate instance, the thermal degradation results in the loss of desirable physical properties of the blend.

The physical properties used to measure the effect of polymer and heat history on the SBS/asphalt blend included:

- Softening point, ASTM D 36.
- Penetration, ASTM D 5.
- Brookfield viscosity at 187.8°C (370°F).
- Young's Modulus, ASTM D 412 (test conditions), initial slope of the stress/strain curve.
- Low temperature flexibility—Single Ply Roofing Institute (SPRI)—method using a 24.4mm (1 inch) by 152.4mm (6 inch) long sample bent through 180° bend in two seconds over a 25.4mm (1 inch) mandrel.

The condition of the polymer as was determined through gel permeation chromatography using three, 10⁵ Å° columns, tetrahydrofuran as the solvent at a flow rate of 1.0 ml per minute at 30°C, using a refractive index detector. Polystyrene standards were used in the molecular weight calibration. The control, for evaluation of the degradation, was neat polymer. The shape of the polymer peaks, along with the change in molecular weight distribution values as compared to the neat polymer, were used as an estimate of polymer thermal degradation.

A Xenon Arc Weatherometer was used to accelerate and simulate aging of the samples with heat, ultraviolet (UV) light and water. The samples were prepared for the weatherometer in accordance with ASTM D 1669. The weatherometer was operated in accordance with ASTM D 4798 using cycle A of 24; one-hour periods consisting of 51 minutes of light and nine minutes of light and water spray.

MATERIALS

The specific materials used in the experiment included:

- Asphalt—100 dmm penetration asphalt flux.
- Polymer—Linear styrene-butadiene-styrene block copolymer, with a styrene/butadiene ratio of 31 to 69.
- Filler—Calcium carbonate.

COATING FORMULATION

| Material | Percent by Weight |
|--------------------|-------------------|
| Asphalt flux | 63 |
| Linear SBS polymer | 12 |
| Filler | 25 |

LABORATORY EXPERIMENTS

A small group of experiments was designed and conducted in the laboratory to simulate plant conditions. This helped with the design of the plant portion of the experiment. It was necessary to determine the conditions that promote gradual degradation so that plant equipment would not be damaged through total gelation of the batch of filled coating. It was also felt that a more controlled experiment would form a good basis of comparison with the plant scale trials.

A batch size of 2000 grams was used. The total amount of asphalt was added to a one gallon container which was placed in a heating mantle equipped with a temperature controller. The initial temperature of the asphalt was 195°C. The slotted head of a one-half horsepower, high shear mixer was placed in the asphalt with the head near the bottom of the container. At a mixer speed of 1200 rpm, the polymer was added over approximately 10 minutes. After polymer addition was completed, the speed of the mixer was increased to 2800 rpm for 40 minutes until the asphalt/polymer blend was complete as measured by smoothness and UV fluorescence microscopy. The final temperature of the pre-blend was controlled to a maximum of 200°C. A low shear mixer was used to incorporate the filler into the asphalt/polymer pre-blend. A sample was removed from the finished batch and designated Lab-1.

The batch that was to be degraded was held, after filler addition, in a covered container at 200°C for a period of 20 hours. The sample was then removed and designated Lab-2.

PLANT EXPERIMENTAL TRIALS

The plant trials were conducted at the Tremco modified bitumen membrane manufacturing plant located in Cleveland, Ohio. The process is of the Nardini⁴ design and was installed in 1984. The SBS/asphalt coating pre-blend is prepared in one of two, 9100 liter (2400 gallon) vertical high speed mixers. It was subsequently transferred to one of two 10600 liter (2800 gallon) low speed horizontal mixers for incorporation of mineral filler into the pre-blend. The high speed mixers are capable of operating at 300 rpm at full capacity and have two high shear mill units located near the top of the mixer shaft and at the bottom of the mixer shaft. This type of mixer combines the ability of a low shear mixer to disperse the polymer when initially loaded into the mixer containing asphalt and the high shear dispersion capability of a rotary mill. The shear imposed on the blend is not as efficient as that imposed by a rotary mill of the Siefer⁵ type, but significantly higher than a typical low shear design mixer.

The design of the experiment was kept relatively simple in an attempt to collect useful data on a plant scale. The coating formulation used flux grade asphalt, linear SBS polymer and calcium carbonate filler, at a single level. The batch

size of 10600 liters (2800 gallons) was held constant to negate any mass effect or differences in heat transfer rate.

Two conditions of manufacture were used. In the first trial, the coating was prepared by filling the mixer with the full amount of bitumen at 185°C required for the batch. The polymer, in crumb form, was added to the bitumen with agitation at 150 rpm over approximately 30 minutes. Upon completion of the addition of polymer, the speed of the mixer was increased to 280 rpm for approximately two hours. At this point, the polymer/asphalt pre-blend had inverted, as determined through UV fluorescence microscopy. It was smooth and ready for transfer to the low speed horizontal mixer. The temperature of the polymer/asphalt pre-blend at this point in the process was 200°C.

After transfer completion, the filler was added in 1000 pound increments with agitation at 16 rpm. After the filler addition was complete, the batch was mixed for 30 to 45 minutes before pumping to the coating line for membrane manufacture. The temperature of the batch at this point was 175°C. A sample was removed for testing and designated Plant-1.

For the second trial, the same procedure was used, except that the filled coating blend was held in the horizontal mixer without agitation for a period of 18 hours at a mean temperature of 175°C. After 18 hours of holding, the coating was mixed for approximately one hour before transfer to the membrane coating line. A sample of the coating was removed for testing and designated Plant-2.

DISCUSSION OF RESULTS

The results of both the laboratory and plant scale experiments are recorded in Table 1. There was a good degree of similarity in the two sets of data collected in terms of the physical properties measured, as well as the polymer degradation noted in the GPC results. In the case of both the plant and laboratory-prepared coatings, samples when held at elevated temperatures for extended periods tended to have a poorer flexibility failure temperature, a higher viscosity and a higher modulus than the samples prepared with a shorter heat history. These comparative results indicate that polymer/asphalt blends with long heat history exhibit increasing levels of degradation due to a change in the polymer structure. From the data, it is evident that the laboratory-degraded sample, Lab-2, was significantly more degraded than the companion plant sample, Plant-2.

Examination of the companion GPC data for each of the blends indicate that the samples prepared with a relatively short heat history (Plant-1, Figure 1 and Lab-1, Figure 2) have a molecular weight distribution similar to the neat polymer, Figure 3.

The GPC results for the long heat history samples reveal a significantly different molecular weight distribution (Plant-2, Figure 4 and Lab-2, Figure 5). From the molecular weight distribution of the polymer, it is probable that the polymer is changing through initial chain scission as evidenced by the increase in the low molecular weight fraction, with subsequent recombination and/or crosslinking. The increases in the higher molecular weight fraction of the distribution, the Young's Modulus and the viscosity are all attributed to higher molecular weight species being formed through thermal degradation.

Table 2 lists the molecular weight averages to complement

the molecular weight distribution curves (Figures 1 through 5). The general trend indicates an increase in both low and high molecular weight fractions. The increase in lower molecular weight fractions is evidenced by the decrease in number average molecular weight, M_n . The calculation for M_n is skewed to lower molecular weight fractions. The increase in higher molecular weight fractions is evidenced by the increase in the weight average, M_w , and the z-average, M_z , molecular weights. The calculation for both of these molecular weight averages is skewed to higher molecular weight fractions.

This mode of degradation, indicated by a trend toward higher molecular weight fractions, is different from other previous work which involved heating the polymer/asphalt blends in a 70°C ventilated oven for up to six months.⁶ It is also different from results obtained on naturally aged granule surfaced membranes.⁷ In both cases, the trend indicated by GPC results was toward lower molecular weight fractions indicating primarily chain scission induced by heat aging as well as natural aging.

Several commercially available granule surfaced SBS modified bitumen products were purchased and tested for condition of the polymer as purchased. Figure 6 shows a product with no indication of thermal degradation of the polymer during manufacture. Figure 7 shows a product that is severely degraded as evidenced by the shape of the peaks and molecular weight values. Both products were manufactured from a similar type branched SBS polymer as identified through GPC analysis. The difference in the condition of the polymer as a result of the difference in the manufacturing operations is quite obvious. These two examples represent two extremes found in the limited study of commercially available SBS modified products.

The final part of the project involved a limited Xenon Arc Weatherometer study of the two sets of coating. Some initial difficulties were encountered in preparing the weatherometer panels from the coating samples. Limited shrinkage of the best films of the coating on the aluminum panels, as a result of panel preparation problems, made determination of the failure point difficult. The panels, with varying amounts of time in the weatherometer, were examined qualitatively and the results are shown in Photos 1 and 2.

Photo 1 shows the difference in the plant samples of standard coating (Plant-1) after 2850 hours and degraded coating (Plant-2) after 2000 hours. There are a significantly greater number of holes representing failure of the coating in the degraded sample with fewer hours in the weatherometer when compared to the non-degraded sample. The surface cracking is also more severe.

Photo 2 shows the difference in the laboratory prepared samples of standard coating (Lab-1) after 1500 hours and the degraded coating (Lab-2) after only 1100 hours. It is evident that the degraded sample shows significantly more deterioration from the accelerated weathering as evidenced by the severe cracking through the film of coating down to the metal panel surface.

CONCLUSIONS

It is reasonably evident from the limited experimental results from both the plant trials and laboratory scale work presented here, and the GPC analysis of two commercially avail-

able SBS modified products, that not all products leave the factory in the same condition. Even in the case of an SBS modified coating that is chemically excellent in terms of polymer/asphalt compatibility, the effect of the manufacturing operation leaves an indelible mark on the product.

From the physical testing as well as the GPC analysis, it can be concluded that products manufactured with coating which has experienced significant thermal degradation during the manufacturing operation may be predicted to leave the factory with poorer physical properties than those produced with a non-degraded coating. It may also be predicted that the products manufactured with thermally degraded coating further degrade due to weathering at a faster rate than products manufactured with non-thermally degraded coating.

To complete the study, the membranes manufactured from these coatings must be naturally weathered. Only after this weathering and subsequent analysis of the coatings will it be possible to determine if thermally degraded coating, in fact, leads to premature failure of the product as used.

ACKNOWLEDGMENT

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REFERENCES

- ¹ Van Gooswilligan, G. and Vonk, W.C., "The Role of Bitumen in Blends with Thermoplastic Rubbers for Roofing Applications, Proceedings of VI International Conference Roofing & Waterproofing, International Waterproofing Association, London, 1986.
- ² "Finaprene Rubbers for Bitumen Modification", Petrofina S.A. Chemical Sales Division, Brussels, Belgium, not dated. "Preparing Blends of Cariflex TR and Bitumens, Shell Elastomers Technical Bulletin TR 6.5, Shell Chemical Company, Houston, Texas, not dated.
- ³ "Mixers for Cariflex TR—Bitumen Blends", Shell Elastomers Technical Bulletin TR 6.3, Shell Chemical Company, Houston, Texas, not dated.
- ⁴ Nardini spa Construzioni Meccaniche, Mignagola di Carbonera - Treviso, Italy, not dated.
- ⁵ Siefert of North America, Division of Boldt Associates, Des Moines, Iowa, not dated.
- ⁶ Marechal, J., "Methods For the Study of Aging of Bitumen-Polymer SBS Materials", Durability of Building Materials, 1, Elsevier Scientific Publishing Company, Amsterdam, 1983, p. 201-208.
- ⁷ Diebold, T., "Polymer Modified Bitumen SBS vs APP", Soprema Technical Note No. 88/779, March 1988.

| Sample | Softening Point, °C | Penetration @ 25°C, dmm | Flex Failure Temperature, °C | Viscosity @ 187.8°C, cP | Modulus, @ 25°C, kPa |
|---------|---------------------|-------------------------|------------------------------|-------------------------|----------------------|
| Plant 1 | 118 | 23 | -40 | 6,150 | 467 |
| Plant 2 | 118 | 21 | -35 | 7,280 | 636 |
| Lab 1 | 117 | 20 | -38 | 6,600 | 359 |
| Lab 2 | 120 | 18 | -28 | 18,000 | 758 |

Table 1 Physical properties of SBS/asphalt blends.

| Sample | M_n | M_w | M_z |
|---------------------|---------|---------|---------|
| Plant 1 | 126,500 | 153,500 | 182,000 |
| Plant 2 | 124,500 | 168,700 | 234,000 |
| Lab 1 | 131,700 | 161,800 | 202,000 |
| Lab 2 | 130,000 | 302,100 | 703,000 |
| Linear Polymer Neat | 127,100 | 165,900 | 185,000 |

Note: These figures represent an average of three runs on each sample and were taken directly from the integrator data. The data on the corresponding molecular weight distributions represent one of the three test runs.

Table 2 Molecular weight distribution results.

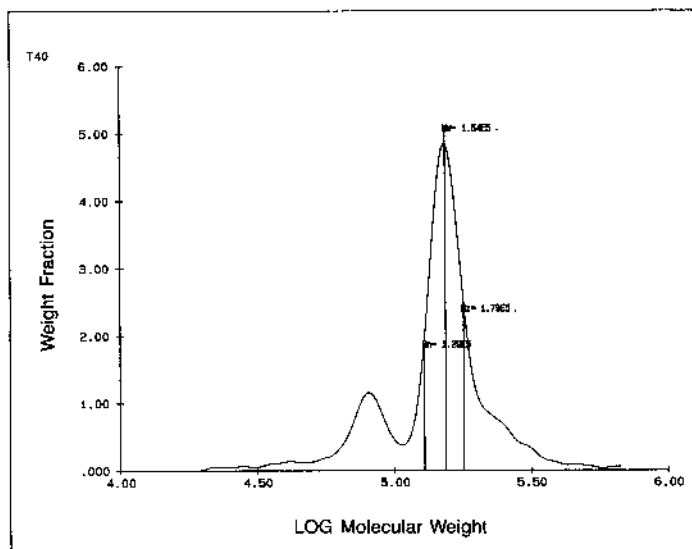


Figure 1 Molecular weight distribution—Sample: Plant-1.

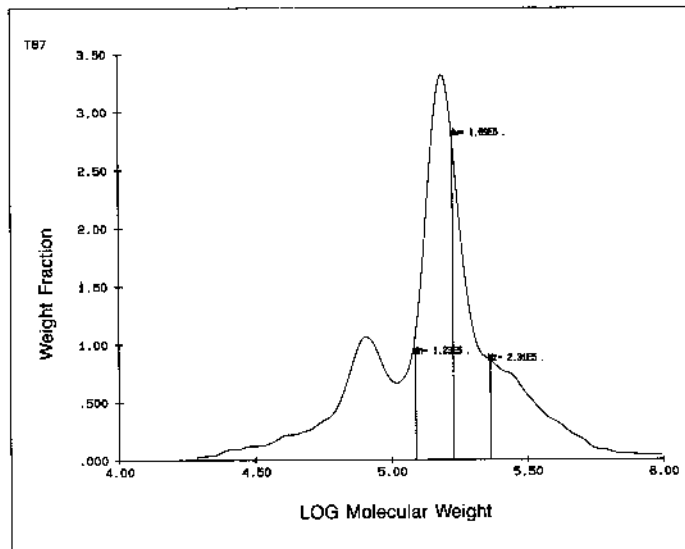


Figure 4 Molecular weight distribution—Sample: Plant-2.

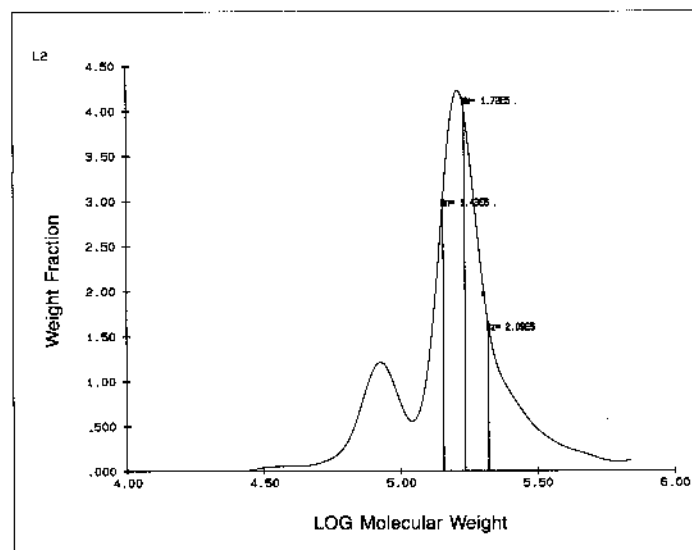


Figure 2 Molecular weight distribution—Sample: Lab-1.

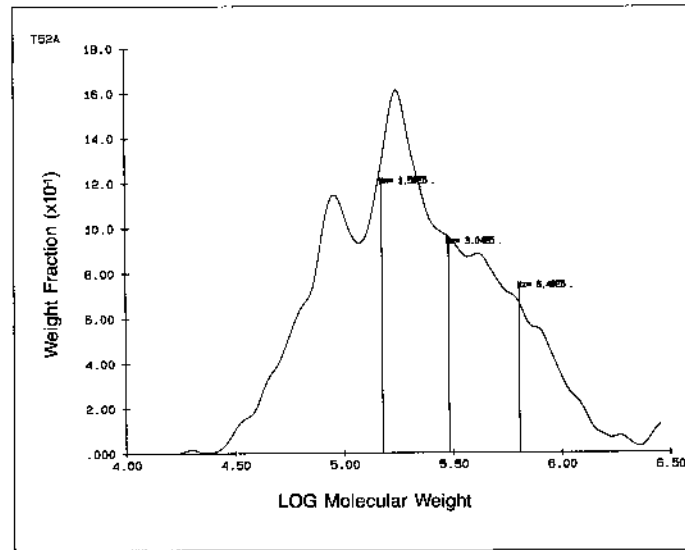


Figure 5 Molecular weight distribution—Sample: Lab-2.

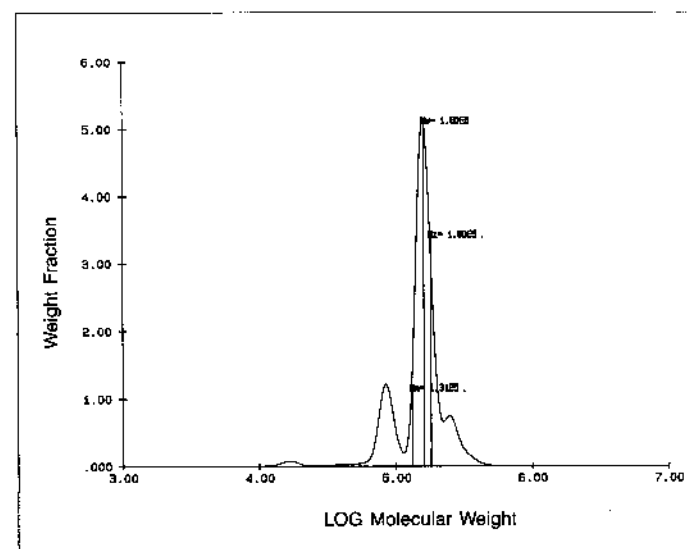


Figure 3 Molecular weight distribution—Sample: linear neat polymer.

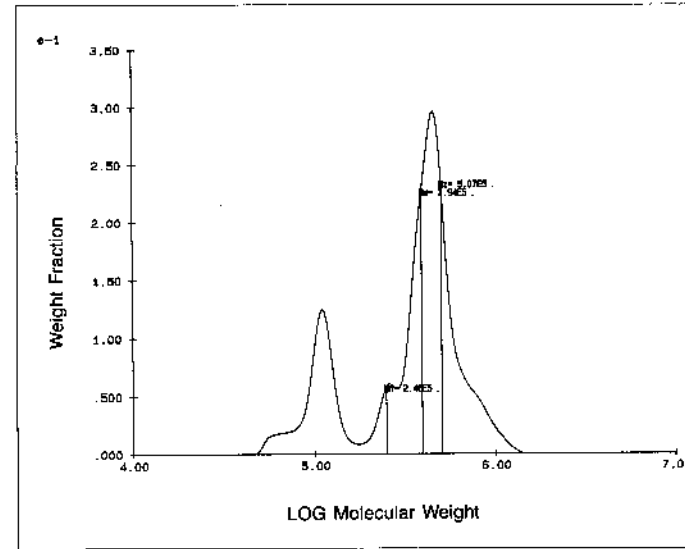


Figure 6 Molecular weight distribution—Sample: commercial product (non-degraded).

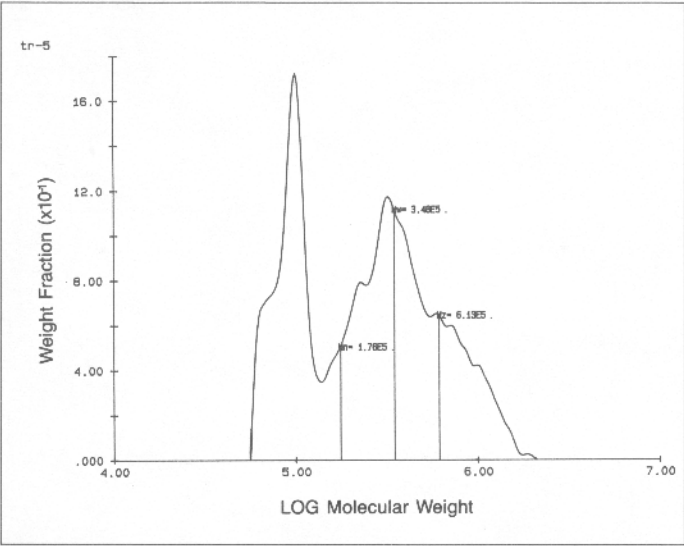


Figure 7 Molecular weight distribution—Sample: commercial product (degraded).

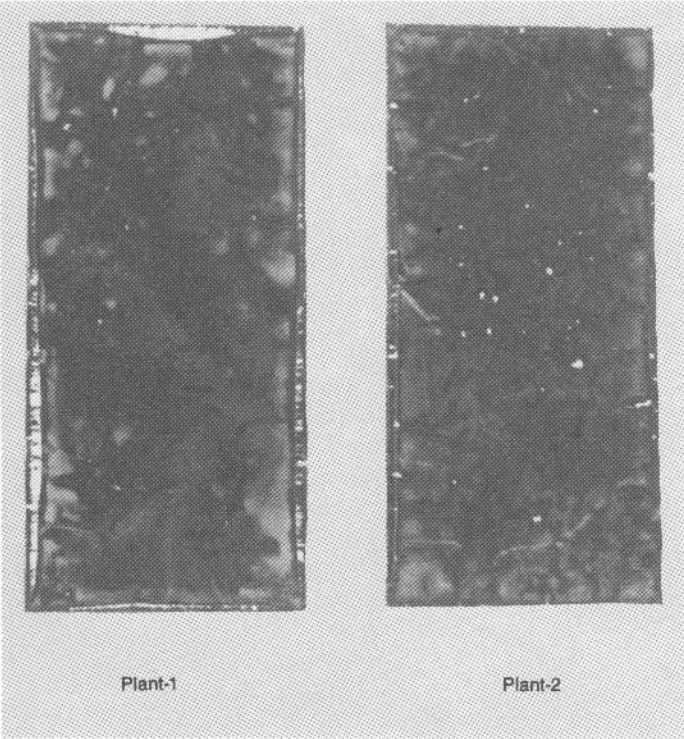


Photo 1 Difference in the plant samples of standard coating (Plant-1) and degraded coating (Plant-2).

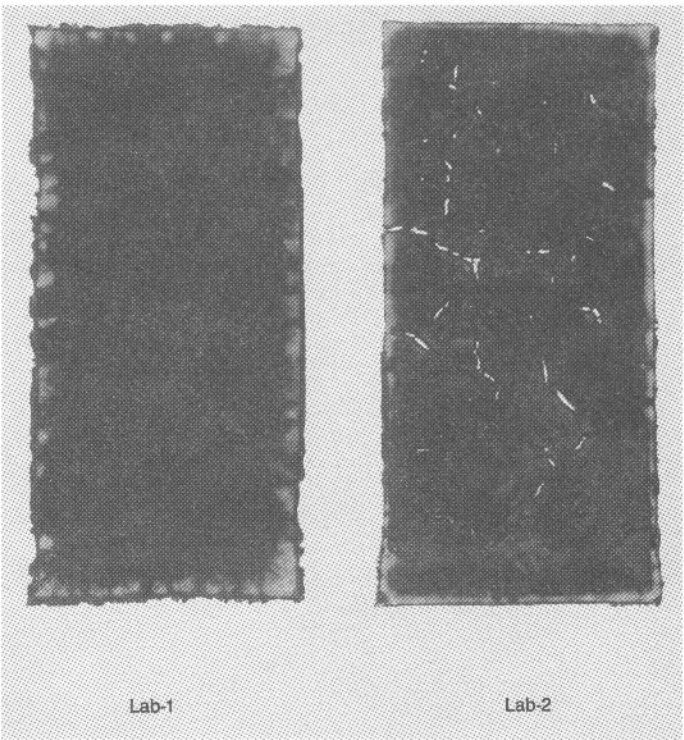


Photo 2 Difference in the laboratory prepared samples of standard coating (Lab-1) and degraded coating (Lab-2).