MODIFIED BITUMEN BLEND TECHNOLOGY

By Tim Kersey

ABSTRACT

This paper deals with modified bitumen roofing materials and focuses specifically on the blend component composed of asphalt, polymers, and extenders. For more than 30 years, the two primary polymer types utilized in modified bitumen roofing blends have been styrene-butadiene-styrene (SBS) and atactic or amorphous polypropylene (APP). In more recent years, polymers such as styrene-ethylene-butylene-styrene (SEBS) and amorphous polyolefins (APO) have also been used in some modified bitumen roofing products. The one component in modified bitumen roofing products that remains constant regardless of polymer type is asphalt. Asphalt is the majority component of modified bitumen, and because of that, its chemistry must be understood to appreciate its impact on the performance of the blend and ultimately on that of the roofing membrane.

Modified bitumen roofing in the United States can no longer be considered a new system. Modified bitumen roofing products are now "thirty something" when their worldwide use is taken into consideration. To quickly review, both SBS and APP modified bitumen roofing were born in Europe in the late 1960s (Laaly 1991). SBS was developed in France and APP in Italy. Today, modified bitumen enjoys the majority market share in many European countries. In the mid-to-late 1970s, these products were introduced onto the U.S. market, and domestic production began. The market has matured, and modified bitumen is an established roofing membrane system. Even so, the products are still misunderstood.

No matter the manufacturer's name, polymer type, reinforcement, or surfacing, the most important component in a modified bitumen sheet is the blend. It is the blend component that is expected to endure the hardships imposed by man and nature for years on end without allowing water to enter a building. The modified bitumen blend, or compound, consists mainly of asphalt, polymer, and filler(s). Some blends may have antioxidants or other stabilizers. The quality of the blend is paramount to the longevity of the modified bitumen roofing membrane. This can, in fact, be said of any roofing membrane type. The quality of polymeric blends used to fabricate thermoplastic and thermoset single ply roofing, and the quality of asphalt used in the construction of BUR are key to the service life that one can expect of the respective finished roofing membrane.

Since the blend is the key waterproofing ingredient in modified bitumen roofing membranes, it is important for industry professionals to understand the makeup of this component. As mentioned earlier, modified bitumen blends have several constituents, but the major ingredient is asphalt. Not only is asphalt the major ingredient in terms of overall percent by weight in the blend, but it is also the most critical of ingredients from a performance standpoint. Some may be under the impression that asphalt is asphalt, but for modified bitumen blends nothing could be further from the truth. Asphalt's chemical composition, not its physical properties, dictates the ultimate quality of any modified bitumen blend. This has been discussed by many authors: Meynard, Rodriguez, Usmani, Laaly, and Halasz to name a few.

The principal output of petroleum refineries can range from light hydrocarbons such as gasoline to heavy lubricating oils or, in some rare cases, asphalt. Petroleum asphalt is a byproduct of the refining process. With some exceptions, refineries sell the asphalt flux to other companies for further processing. Some large refineries have discontinued the sale of asphalt flux altogether; it is fired and sold as coke.

Since asphalt is a byproduct, how are its chemical characteristics controlled? Two major factors determine asphalt quality: refining process and crude oil source. The same crude oil supply can yield various percentages of hydrocarbon "streams" or types when processed by different refining techniques. This is a simplistic explanation, as the refining process is highly complex. Crude oil chemistry varies by geographic location or oil field, which in turn dictates the asphalt's chemistry. No matter the refining process, some crude oil chemistry is not suited for polymer modification.

Asphalt is a heavy hydrocarbon composed of a multitude of chemical groups. To better understand its structure, it is broken into chemical fractions determined by chromatographic methods, e.g., Iatroscan or HPLC (high performance liquid chromatography). These fractions are commonly published as: Asphaltenes, Resins, Cyclics, and Saturates. (See *Figure 1*.)

The resins, cyclics, and saturates can be grouped together and referred to as the maltenes fraction (Barth 1962). Asphaltenes are the heavy, carbon black-like molecules that are insoluble in pentane or heptane, and give asphalt its softening point and "body." Maltenes, on the other hand, are the oily portions of the asphalt that give it pliability. In order for asphalts to function well with modifiers, these fractions must be optimized for polymer modification. For example, asphalt used for polymer modification must have a relatively low asphaltene percentage, generally between 7 and 10%; but this is only one of many considerations.

Before modern-day polymer-modified bitumen, asphalt was modified for centuries by other means. Naturally-occurring

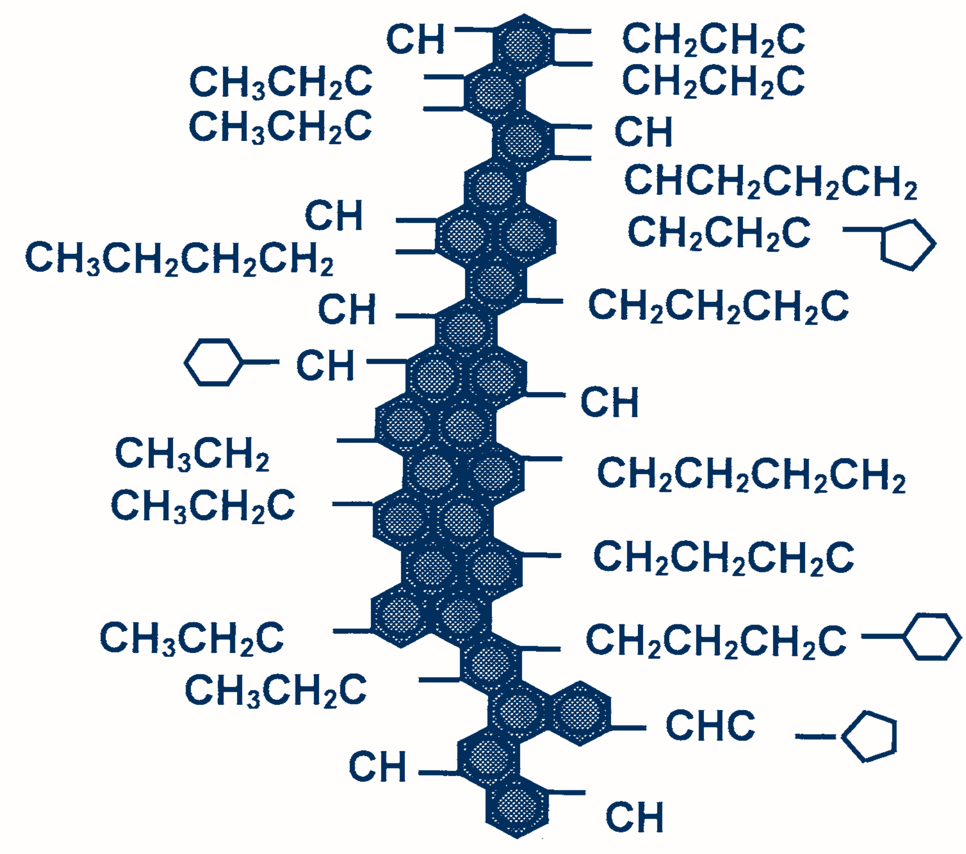

Figure 1: Postulated Structure of Asphaltenes

asphalt was known to be a very good waterproofing agent, and the simple addition of straw or other fiber widened its application range. Since 1894 (Abraham 1920), asphalt flux has been modified chemically by forcing air through it. The end product is called oxidized or blown asphalt. Again, stated simply, this process involves blowing air through pipes to the bottom of an asphalt tank where it is bubbled to the top under controlled conditions. An exothermic oxidation reaction occurs, and the soft, low viscosity asphalt flux is transformed into products that are well known in the roofing business. Lower molecular weight maltene fractions are polymerized and basically converted to asphaltenes. For example, asphaltenes increase from about 10% in a raw flux to about 30% in an ASTM D-312, Type III or Type IV oxidized asphalt.

Figure 2 shows the typical softening point and low temperature flexibility for a soft flux and Type IV oxidized asphalt. Although oxidation enhances asphalt flux by increasing the softening point to withstand rooftop conditions, there is a definite downside to this means of modification. In aging, the term oxidation generally carries a negative connotation, and the same can be said of oxidizing asphalt. Properties are enhanced in some ways, but at the same time, aging of the flux is accelerated. Oxidized asphalts are not good candidates for polymer modification due to the high asphaltene content. The asphaltene and oil fractions are in a gel structure and are not as receptive to blending with the polymer. (See *Figure 2*.)

Another popular type of asphalt modification is the addition of solvent with fibers, fillers, and stabilizers to make solvent-based cutback products. One of the best fibers for cutback products was asbestos, because it provided slump resistance and strength while at the same time prevented solvent and solids from separating or flushing in the pail. When asbestos was phased out, other chemical stabilizers had to be added to the cutbacks to prevent flushing. Cutbacks are gaining popularity as an adhesive, in lieu of hot asphalt, for installing modified bitumen roofing membranes.

Modified bitumens as we know them today are of the polymer-modified variety. Though others have been previously acknowledged, there are two basic types of modified bitumen roofing: elastomeric (SBS) and plastomeric (APP). In both cases, soft flux-type asphalt is used for polymer modification. That is where similarities should end. Asphalt chemistry cannot be optimized so that it is suitable for modification with both SBS and

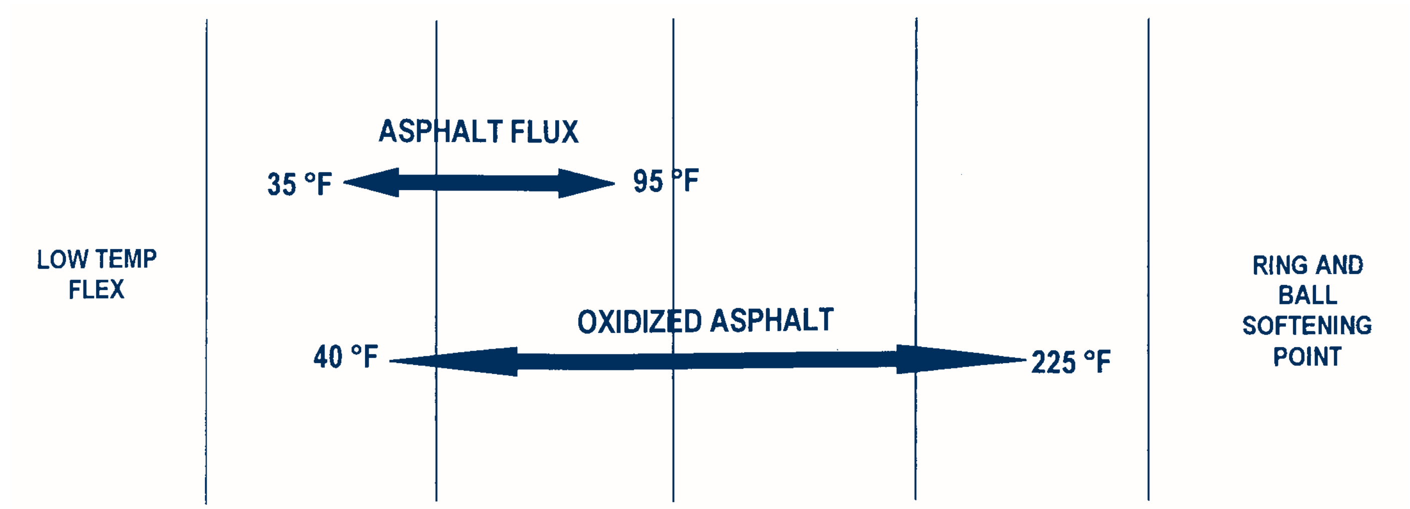

Figure 2: Serviceability Range

APP. A single asphalt could be used for both SBS and APP, but the quality of one or both of the blend types would be sacrificed. If long-term performance is the objective, asphalt flux chemistry must be adjusted so it is best formulated for either SBS or APP modification.

When long-term aging effects are taken into account, the evaluation and selection of asphalt for use with SBS or APP is a process that takes several months to a few years. Regarding SBS-modified bitumen, once the asphalt chemistry is evaluated and selected for a specific SBS polymer, there should be no need for batch-to-batch blend alterations. This is, of course, contingent upon maintaining consistent asphalt supply and chemistry day-in and day-out. The manufacture of SBS polymers is quite sophisticated, and quality companies can supply extremely consistent polymer. Since the processing of SBS elastomers is very controllable, SBS molecules can be tailored to meet specific softening points and low temperature properties. After an SBS polymer profile is selected, asphalt chemistry should remain consistent to ensure that every batch performs the same. Modified bitumen companies that have consistent asphalt supplies with known chemical properties will likely supply roofing materials with consistent properties (that is, if process parameters are appropriate and consistent).

APP asphalt modification can be approached differently depending on the supply of polymer. Initially, APP plastic was merely a byproduct of isotactic polypropylene plastic (IPP) manufacturing; therefore, properties of the APP polymer could vary from shipment to shipment. Modified bitumen producers test incoming APP raw materials, ascertain their properties, and batch ingredients are adjusted accordingly. Many APP-modified bitumen blends are a mixture of APP and IPP and/or other copolymers. It is for this reason that some say that APP-modified bitumen is more difficult to produce consistently than SBS. It is not that the chemistry is more complicated; rather it is the need for frequently adjusting blend components to compensate for inconsistency in incoming raw material. Byproduct APP is still in use today, but there are companies providing on-demand APP polymer that is more consistent and more costly than the byproduct polymer (Usmani 1997). This reduces the necessity to adjust batch-to-batch formulations.

SBS is known in the business as a thermoplastic elastomer or TPE. Since it is a synthetic rubber, SBS truly imparts an elastic nature to asphalt when blended properly. SBS is typically added to asphalt in quantities ranging from 11 to 15% polymer-to-asphalt ratio, but this is dependent on the molecular design of the SBS polymer. It can provide elongation values of greater than 1500%, but more importantly, it can recover to its original dimensions after being subjected to prolonged extension. This property is called permanent set or elastic recovery and is indicative of the material's response to rooftop-related stresses such as thermally- and mechanically-induced expansion/contraction. This test is performed only on the blend, not the sheet material. SBS blends can have permanent set values exceeding 200% when new and near 25% after aging for six months at 70°C (Fabvier 1995) which correlates to approximately 30 years in the field. If an SBS blend has good permanent set characteristics during its service life, it can be used with all types of reinforcement, including fiberglass, polyester, and any combination thereof. SBS blends with marginal permanent set properties and/or poor aging qualities should be more heavily reinforced to help compensate for any blend deficiencies.

One flaw found in some SBS blends is overuse of filler. High filler percentages are sometimes used to provide fire resistance to the finished roofing membrane or to reduce cost. Problems arise when filler percentages creep higher than 35% by weight of the blend component. As filler exceeds this level, the permanent set or elasticity of the blend is adversely affected (Morgan and Mulder 1995). (See *Figure 3*.)

The blend may remain very flexible at first even though there is too much filler, but the performance and service life of the membrane will suffer. Fire ratings can be achieved without high filler percentages. Regardless of percentage, filler used in these compounds should be inert. Some fillers carry trace elements that can actually accelerate the aging process of the blend, thus reducing life expectancy (Diebold 1985). (See *Figure 3*.)

APP enhances asphalt with a plastomeric quality. There are different grades of APP available, and the polymer-to-asphalt ratio can vary from 20 to 30% APP to asphalt depending on the polymer raw materials. APP modified bitumen blends have a permanent set value of less than 10% when new and this value declines with aging. In the past, it was generalized that APP had a higher softening point and higher flexibility temperature than SBS. Today, SBS blends can be customized to give softening points similar to those of APP blends, but SBS retains the lower flexibility temperatures. (See *Figure 4*.) The old adage that APP was more suitable for warm climates and SBS for cold climates is purely an adage.

The question of failure mode of modified bitumen has been broached from time to time, and some explanation can be given for the component addressed herein: the modified bitumen blend. Failure of the modified bitumen blend can stem from a

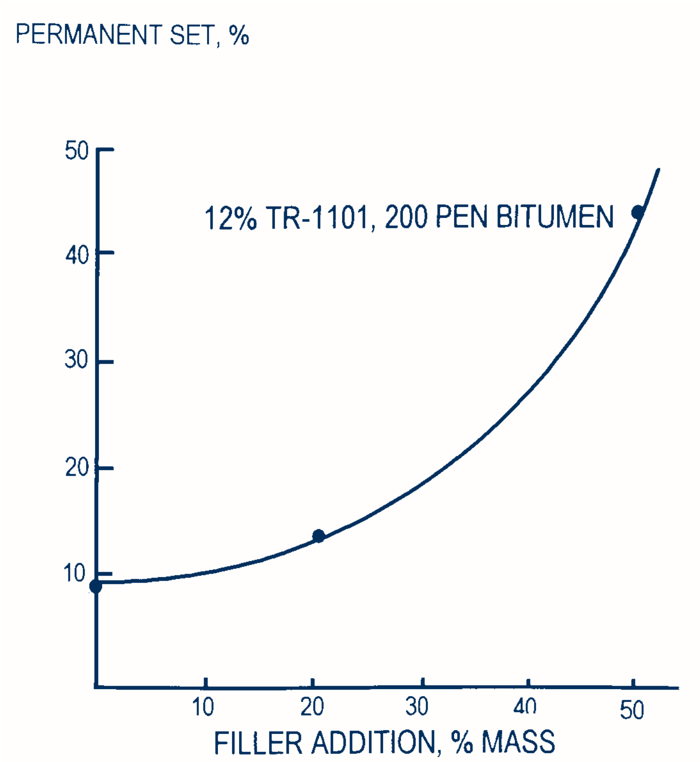

Figure 3: Permanent Set

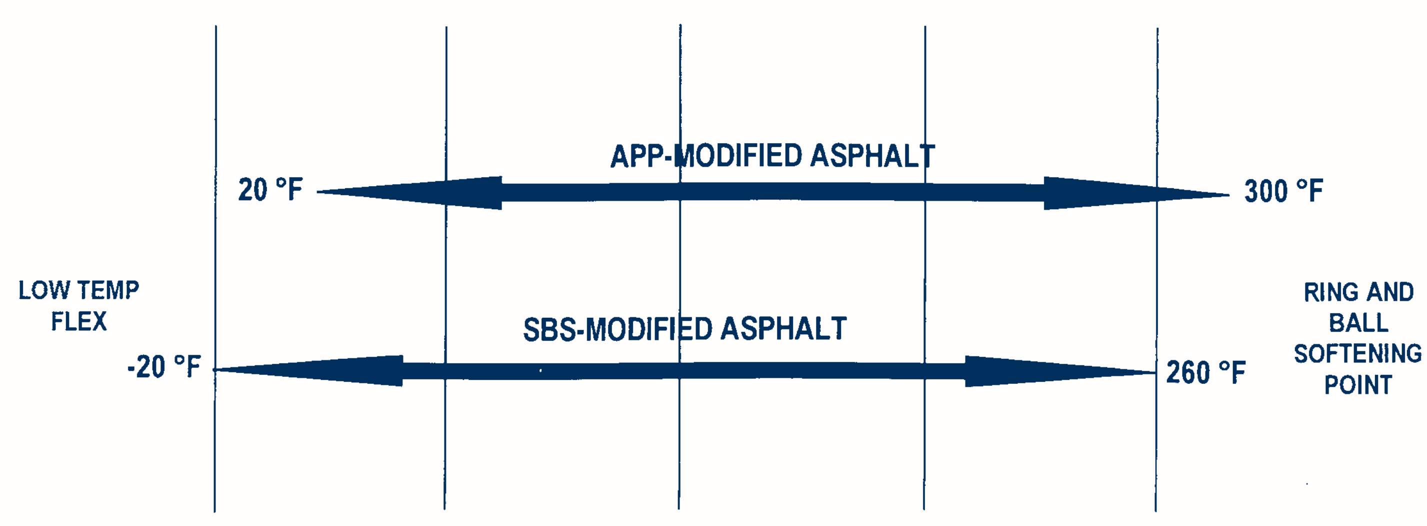

Figure 4: Serviceability Range

number of sources, including, but not limited to: poor asphalt/polymer compatibility, poor formulation ratios of polymer and asphalt, poor quality polymer, too much or the wrong type of filler, mixing temperature and conditions, and mixing and/or storing blends at high temperature for too long. Failure may manifest itself in as many forms, some of which are not detectable until long after the roofing membrane is installed. Catastrophic failure, e.g., total phase separation of asphalt and polymer, is apparent on the roof, but less dramatic premature failure can go undetected.

If blended properly, the long-term failure mechanism of SBS-modified bitumen in particular is the scission of double bonds found in the polybutadiene mid-block of SBS. For this to occur, the product must be subjected to heat and oxygen. For properly designed SBS blends, this is a slow process that can be traced using Gel Permeation Chromatography to analyze changes in the molecular weight distribution of the SBS molecule over time (Meynard 1982). Service life of SBS-modified bitumen blends can be predicted by correlating test results from artificially heat-aged samples with samples taken from roofs. This is, of course, dependent upon factors such as geographic location, building design and use, insulation types and thickness, etc. Correlations were shown for SBS-modified bitumen roofs in Europe and the United States (Duchesne 1991) and (Duchesne, et al, 1997). Heat aging at 70° C for six months and 80° C for 3 months was projected to approximate 30 years of field exposure.

In summary, the modified bitumen blend is the waterproofing element of modified bitumen roofing materials, and asphalt is the key ingredient in the blend. Selection of raw materials is indeed critical to making high-quality modified bitumen blends, whether SBS or APP. In order of importance, the criteria for raw material selection should be:

- Asphalt chemistry tailored for the polymer of choice.
- Polymer selected for optimum properties and consistency.
- Filler that is inert and used in appropriate quantities.
- Fire retardants that do not adversely affect aging properties.

Manufacturing processes should be optimized to ensure that:

- Mixing equipment is designed for the intended modified bitumen blend.
- High shear mixing of SBS does not initiate polymer breakdown.
- Heat is controlled to minimize polymer deterioration during mixing.
- Blend storage at high temperature is minimized (or evacuated of oxygen when held for extended periods).

Testing of these products could be the subject of a separate paper, but some of the more important physical tests for modified bitumen blends are:

- Ring-and-ball softening point.
- Penetration at various temperatures.
- Compound stability.
- Low temperature flexibility.
- Elastic recovery (permanent set).
- Ultimate elongation.
- Heat aging resistance.
- Fatigue resistance.

Popular analytical testing may include:

- UV fluorescence microscopy.
- Gel permeation chromatography.
- FTIR (Fourier Transform Infrared Spectroscopy).
- Numerous other chemical and mechanical techniques.

When all these variables are taken into account, the odds of haphazardly producing a high-quality modified bitumen blend on a consistent basis are astronomical. Modified bitumen roofing is neither "black art" nor "low tech." It is a construction science that requires intricate chemical knowledge of asphalt and polymers to produce blend components that last more than two decades in all climatic and environmental conditions.

It was beyond the scope of this paper to address other modified bitumen sheet components. Reinforcements and surfacing materials play secondarily important roles in modified bitumen compared to the blend, but should not be disregarded. This is another topic for another time.

Some roofing professionals may view this narrative as too focused and detailed regarding only one component of the modified bitumen roofing membrane. Keep in mind, no matter the type of waterproof roofing membrane, it is this blend component that plays a vital role in the long-term performance of the roofing membrane. It keeps the water out of the building. ■

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