

AGING OF POLYALPHAOLEFINIC MODIFIED BITUMEN FOR ROOFING MEMBRANES

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This paper attempts to rationalize the actual knowledge on the action mechanism of polymers—specifically polyalphaolefins (PAO)—added to bitumen to produce waterproofing membranes and the aging performance of the resulting compounds.

The modification of bitumen with PAOs is based on the preferential absorption by the polymer of saturated and low molecular weight aromatic bitumen constituents.

Aging of PAO-bitumen compounds is the result of changes in the bitumen and the polymer induced by environmental factors like temperature, oxygen and UV radiation. Chemical changes in the aged bitumen and excessive crystallinity of the PAO polymer can lead to a gradual demixing process between the polymer and absorbed bitumen constituents, resulting in a discontinuous polymeric matrix and loss in low temperature flexibility. High molecular weight PAOs with moderate crystallinity counteract this demixing phenomenon and tend to improve aging resistance of PAO modified bitumen.

Accelerated thermo-oxidative aging performed under appropriate conditions are shown to be sufficiently severe to allow a relevant prediction of the real life performance of PAO-bitumen systems with time. This is not valid for SBS modified bitumen. The possibility to predict the change in behavior of PAO modified bitumen by means of accelerated thermal aging permits to target PAO roofing to specific environments.

KEYWORDS

Bitumen modification, cold flexibility, continuous polymeric phase, crystallinity, molecular weight, oil absorption, polyalphaolefins (PAO), roofing membrane, thermo-oxidative aging, UV aging, waterproofing, weathering.

INTRODUCTION

Since the discovery of the possibility to modify distilled bitumen with polymers and the birth of prefabricated asphalt roofing membranes about 25 years ago in Italy, the market growth of these products has been enormous.

Until today, only two families of polymers have found a significant application in this domain, i.e., amorphous polyalphaolefins (APAO) and block copolymers of styrene and butadiene (SBS). In this context the notion 'APAO' refers to (1) atactic polypropylene homopolymers, (2) atactic copolymers of propylene and ethylene, (3) atactic terpolymers of propylene with higher alphaolefins (4 to 8 carbon atoms) and ethylene and (4) mutual blends of these polymers. In Italy, bitumen modified with, APAO covers 95 percent of the 80 million square meter roofing market. In the U.S. where the polymer modified membranes appeared in the last decade, production is estimated between 50, and 60 mil-

lion square meter, of which APAO modified bitumen represents 70 percent.

As in most industrial sectors, today there is a growing preoccupation toward product quality. Since waterproofing systems are intended to have the longest possible service life, one of the most critical quality features is the aging performance. It is known that the deterioration of polymer modified bitumen with time is inversely proportional to the polymer content of the blend. The actual tendency to reduce costs on the other hand has created the necessity to produce reliable roofing membranes with the lowest possible polymer content. As a result, the importance of aging tests is steadily growing.

This paper will attempt to rationalize the present knowledge on the action mechanism of polymers—specifically polyalphaolefins (PAO)—added to bitumen and the aging performance of the resulting blends.

MODIFICATION OF BITUMEN WITH POLYALPHAOLEFINS

Composition of Bitumen

A bitumen can be separated into four generic fractions by chromatographic techniques:

- Saturates—aliphatic, naphthenic or combined aliphatic-naphthenic hydrocarbons (molecular weight: 300-500).
- Aromatics—molecules containing aromatic rings with paraffinic or naphthenic side chains (molecular weight: 300-2,000).
- Resins—molecules containing many aromatic rings with paraffinic or naphthenic side chains; presence of heteroatoms (oxygen, nitrogen and sulphur) leads to various polar groups like hydroxyl, amine, carbonyl, carboxyl, sulfide, etc. (molecular weight: 500-50,000).
- Asphaltenes—molecules containing polycyclic aromatic rings with paraffinic or naphthenic side chains; due to the higher content of heteroatoms, the asphaltenes are more polar than the resins (molecular weight: 1,000-100,000).

Bitumen is considered to be a colloidal system in which the constituents with the highest molecular weight and polarity (the asphaltenes) form the dispersed phase, while the mixture of saturates and aromatics represents the continuous phase. The resins act as dispersing agents stabilizing the system. In this study, a straight run bitumen was used with a penetration value of 190 dmm at 25°C (ASTM D.5) and the following composition was determined by thin layer chromatography:

Saturates	8.1 percent
Aromatics	52.8 percent
Resins	20.5 percent
Asphaltenes	18.6 percent

Elemental analysis of bitumen further indicates the presence of metals like iron, nickel and vanadium. These are believed to be present in a complexed state (porphyrinic type structures).

Mechanism of Bitumen Modification with Polymers

What is commonly referred to as "compatibility of a polymer with bitumen," can be translated into the capacity of this polymer to absorb a certain portion of the bitumen constituents which is sufficient to yield an extended polymer matrix with uniform and well separated residual bitumen particles, stable over a useful time-temperature range. The more the polymer-bitumen system responds to these criteria, the better their mutual compatibility. The polymer concentration at which a continuous polymeric phase is formed, is determined by the nature of the polymer, the composition of the bitumen and the processing (mixing) conditions.

As an example, the process of blending 25 parts of an amorphous polyalphaolefin (APAO) with 75 parts of bitumen (penetration 190) is described. The mixing is performed at 180°C under continuous stirring (propeller 200 rpm). The evolution of the blend in function of mixing time is monitored by UV fluorescence microscopy (Figure 1). In the first stages of the mixing process a dominant black phase of bitumen with irregular yellow-white isles of PAO is observed. The yellow phase progressively gains in volume and eventually becomes predominant and continuous. As evidenced by many authors, the yellow phase now consists of virtually all the PAO polymer, a large part of the saturates and aromatics, and a minor portion of the resins. The residual bitumen is formed by virtually all the asphaltenes, the major portion of the resins and the remaining saturates and aromatics.

The generation of a continuous polymeric phase (residual bitumen embedded in the polymer matrix) is fundamental for a good bitumen modification which has to fully reflect the properties of the polymer and results in improved flexibility and reduced temperature susceptibility.

Table 1 data indicate that the cold flexibility (DIN 52123) of the APAO-bitumen compound is highly sensitive to the existence of a continuous polymeric phase, while penetration and softening point are less dependent.

Different polymers have been studied in bitumen and it was found that all polymers capable to absorb bitumen constituents with no or weak polarity (mainly saturates and aromatics) can modify bitumen. The final characteristics of the polymer-bitumen blend are largely determined by the polymer being used.

A useful correlation was found between the capacity of a polymer to absorb paraffinic or aromatic oils and the compatibility of this same polymer with bitumen, as partly shown in Table 2. The oil absorption capacity was determined by a semi-quantitative test. Paraffinic oil was mixed with the polymer at high temperature (180°C) in discrete concentrations. The maximum level of oil for which the blend at room temperature showed a solid aspect without visual exudation of the oil, was considered as the oil absorption capacity and is expressed in percent; the polymer mass being equal to 100 percent.

Performing this oil absorption test to a series of polymers has shown that over time the oil is expelled by the polymer. The severity of oil exudation is related to the degree of crystallinity, the polarity and the molecular weight of the poly-

mer. This observation indicates why only sufficiently amorphous and apolar polymers can be used if an acceptable bitumen modification is to be realized. It should be emphasized that the approach of the modification process via the concept of oil absorption capacity is merely qualitative. Indeed, the compatibility of a given polymer with a given bitumen type in the end is determined by the proportions of the four generic fractions in the bitumen. More than PAO, SBS polymers are known to be sensitive to the bitumen composition.^{1,3} Nevertheless, the right choice of the polymer and bitumen type to be combined is extremely important. The final verification is always in practice.

MECHANISM OF AGING OF POLYMER-BITUMEN BLENDS

All polymer-bitumen blends show a change in properties with time, resulting in a product with overall less favorable characteristics. This phenomenon is commonly called "aging." Aging is caused by a complex interaction between different factors which in nature can be external (environment) or internal (related to the blend).

External Factors:

- Temperature
- Oxygen and ozone
- Ultraviolet (UV) radiation
- Humidity
- Mechanical stresses

Internal Factor:

- Components of the blend

This paper focuses on the aging of PAO-bitumen compounds under influence of temperature and UV radiation in an aerated environment. The impact of mechanical stresses has not been considered.

To approach the aging process in a systematic way, three distinct phenomena which together determine the aging mechanism are discussed:

- Chemical changes of bitumen.
- Chemical changes of the polymer.
- Demixing between polymer and absorbed bitumen constituents.

Chemical Changes of the Bitumen

Bitumen is susceptible to aging, which is clearly evidenced by pronounced changes in its mechanical properties with time, e.g., decrease of the penetration, increase of the softening point and the penetration index, increase of viscosity, etc. The intensity of these changes is of course related to the weathering conditions.

As reported in the general literature, following chemical processes are observed when bitumen is aged at 70°C to 80°C in an aerated environment.

Conversion of part of the aromatic fraction towards the resin fraction is the result of the oxidation of aromatic constituents, whereby oxygen is chemically built into the molecule leading to an increased polarity. Simultaneously, condensation reactions lead to an increase in molecular weight.

Conversion of part of the resin towards the asphaltene fraction caused by similar condensation reactions. The increase of the asphaltene fraction after extended thermo-oxidative aging (3 months at 80°C), is in the order of 20 to 40 percent, depending on the bitumen type.

Figure 2 combines the infrared (IR) spectra of bitumen (penetration 190) before and after thermal aging at 80°C in air.

One observes an absorption increase in the region of 3400 to 3150 cm^{-1} (reciprocal wavelength) indicating the formation of bounded hydroxyl groups (-OH). In the 1780 to 1630 cm^{-1} region, the increased absorption is due to the presence of carbonyl (C=O) functionalities (ketones, anhydrides, carboxylic acids and derivatives) formed on oxidation. The increased absorption in the 1620 to 1570 cm^{-1} region is due to an increase of conjugated carbon-carbon double bond vibrations evidence for an increase in aromatic constituents with one or more aromatic rings. Finally, in the 1350 to 1000 cm^{-1} region, several peaks appear resulting from formation of sulfoxides and sulphones.

The changes in the bitumen upon thermo-oxidative aging will have their effect on the polymer-bitumen blend. The most important change in the aged bitumen is the increase in asphaltene content due to "aromatics \rightarrow resins \rightarrow asphaltenes" transformations. Especially in poor formulations, where a relatively low amount of polymer is introduced, this will have a detrimental influence on the continuity of the polymer mix.

The high concentration of aromatic molecules present in the bitumen leads to a strong absorption of UV light. From the literature it is known that UV radiation tends to intensify thermo-oxidative aging of bitumen.

The evaporation of volatile bitumen constituents is believed to have only a minor influence in the case of polymer modified bitumen compounds. Moreover, this volatile bitumen fraction, which usually is of the order of a few percent, is already largely removed during the mixing process. It should be noted that some types of bitumen in the TFOT (Thin Film Oven Test) show a weight increase due to oxidation.⁴

Chemical Changes of the Polymer

It is obvious that the resistance to weathering of the polymer will influence the aging characteristics of the polymer-bitumen compound. Therefore, to be suitable as a bitumen modifier, the polymer should be as inert as possible towards the combined impacts of temperature, oxygen, UV radiation and humidity.

Unsaturated polymers (polybutadiene, SBS, etc.) are known to undergo severe degradation upon weathering, mainly due to their pronounced sensitivity to UV initiated oxidation. This is a radical reaction initiated by UV, but propagated by oxygen or ozone migrating into the bulk of the polymer. Compounded with bitumen, an unsaturated polymer is to a certain extent protected against the negative effects of UV radiation. In the case of SBS, this protection however is not sufficient to prevent, after prolonged exposure to UV radiation, a sudden drastic drop in molecular weight which eventually leads to destruction of the continuity of the polymer matrix, a loss in low temperature flexibility of the polymer-bitumen blend and a worsening of the resistance to higher temperatures (decrease in the softening point). In the absence of mechanical stresses which

can be induced by temperature variations or physical movements of the roof, the degradation is limited to a rather thin layer at the surface. In real life, however, mechanical stresses can always appear and thus it is compulsory to protect the SBS-bitumen membrane from UV light by adding a surfacing, i.e., mineral granules or a coating.

Polyalphaolefins (PAOs), because of their saturated character, form a category of chemically very inert polymers with a relatively high resistance to weathering. PAOs, in contrast to unsaturated polymers, are practically unaffected when exposed to temperatures of 70°C to 80°C in an aerated environment in absence of UV radiation. While PAOs are definitely more resistant to UV than unsaturated polymers, the tertiary hydrogen atoms in the polymer chain and the presence of very low concentrations of terminal double bonds, render the pure polymer susceptible to UV radiation. When a PAO is compounded with bitumen, the polymer remains practically unaffected by UV initiated oxidation. This is explained by the lower transparency of the blend.

The cold flexibility is a sensitive indicator for the aging performance of a PAO-bitumen roofing compound (discussed further in "Significance of Accelerated Aging Tests"). Table 3 illustrates the small change in cold flex after thermo-oxidative aging for three pure PAO polymers.

Demixing Between Polymer and Absorbed Bitumen Components

As discussed previously, the modification of bitumen by polymers is based on the absorption of definite bitumen constituents. In the case of polyalphaolefins, the absorbed constituents are mainly saturated and low molecular weight aromatic molecules. The resins and asphaltenes preferentially remain in the residual bitumen phase due to their higher molecular weight and polarity. Indeed, the asphaltenes, and to a lesser degree also the resins, show a polymeric character and thermodynamically interact with the PAO polymer yielding two separate phases.

The modification of bitumen with PAOs can thus be considered as an extraction of relatively low molecular weight saturated and aromatic hydrocarbons, plus a fraction of the more polar resins, from the bitumen towards the polymer. This 'extraction' is achieved during the mixing process at temperatures well above the glass transition and the melting point of the polymer. The mutual solubility between the polymers and the absorbed hydrocarbons at high temperature (mixing) can be considerably different at roofing service temperatures.

The authors have attempted to evaluate empirically two major parameters affecting this demixing process; the crystallinity and, the molecular weight of the PAO polymer.

Table 4 shows the aging performance of four PAO polymers with different degrees of crystallinity as measured by differential scanning calorimetry (DSC). The evaluated polymers were chemically similar and their average molecular weights estimated by viscosity measurements, were comparable. The blend composition was 25 parts of polymer with 75 parts of bitumen (penetration 190). The cold flexibility and the nature of the dispersion were monitored during thermal aging at 80°C in an air-circulated oven.

The fresh blends in all cases showed a continuous polymeric phase, while the cold flexibility improved with decreasing crystallinity of the PAO polymer. During thermal aging, the cold flexibility of the blends with higher crystal-

linity was substantially reduced and agglomeration of residual bitumen particles was observed. Only the PAO with 21 percent crystallinity lead to a stable blend with bitumen.

Table 5 illustrates the influence of the molecular weight of the PAO polymer on the aging performance. Three chemically similar PAO polymers with a comparable degree of crystallinity of about 15 percent were blended at a high (28 percent) and low (20 percent) concentration with bitumen (penetration 190). The high, medium and low molecular weight PAOs, respectively, had melt viscosities of 1,000,000, 500,000 and 20,000 centipoise (cps) at 190°C. The cold flexibility and dispersion of the blends was monitored during thermal aging at 80°C in an air-circulated oven.

The obtained results indicate that higher molecular weight PAOs impart more flexibility to the blend. All blends with high polymer concentration showed good resistance to thermo-oxidative aging. At lower polymer concentrations on the other hand, the effect of the PAO molecular weight is manifested; the low molecular weight PAO blend shows a drastic change in cold flexibility and dispersion, while surface alterations like oil exudation and blistering were noticed.

The better aging performance obtained with the higher molecular weight PAOs is explained by their higher capacity to retain the absorbed hydrocarbons in the polymer phase. At the same time, the higher viscosity of the polymer matrix counteracts the agglomeration of the residual bitumen particles which is driven by the difference in density between polymer matrix and residual bitumen.

In practice, for various economical and technical reasons, bitumen modification with polyalphaolefins is, for the most part, not made with one single polymer, but with a blend of different PAOs. In these cases also, the mutual compatibility of the polymers used must be evaluated with care to prevent aging problems.

Conclusively, to obtain PAO-bitumen compounds with acceptable resistance to thermal aging in the absence of mechanical stress, the following important parameters should be considered:

- Excess concentration of the polymer in respect of the continuous polymeric phase.
- Crystallinity of the polymer and the resulting blend.
- Molecular weight of the polymer.
- Mutual compatibility when two or more polymers are combined.

SIGNIFICANCE OF ACCELERATED AGING TESTS

It is not an easy task to correlate the real life performance of a roofing membrane with parameters that can be measured in a simulated aging test. Besides the huge variety of environmental conditions and roof structures, the aging performance of the membranes is not only determined by the properties of the polymer-bitumen blend, but by the total construction of the membrane (thickness, type of reinforcement, adhesion between reinforcement and modified bitumen, etc.) Our objective was to identify an accelerated lab test to simulate weathering of PAO-bitumen compounds in a reliable way. This implied the identification of those quantifiable compound parameters which can serve best as an indicator of the aging process, and the determination of the weathering conditions to be imposed.

The parameters which are commonly considered to characterize the physical performance of a roofing membrane or a polymer-bitumen compound are:

- Melt viscosity.
- Penetration at 25°C (ASTM D.5).
- Penetration at 60°C (performing ASTM D.5 at 60°C).
- Softening point, Ring and Ball (ASTM D 2398).
- Cold flexibility (DIN 52123).
- Nature of the dispersion by UV fluorescence microscopy.
- Macroscopic aspect (oil exudation, blistering, cracking, alligating, etc.).

Other mechanical tests like the measurement of the elongation at break and tensile strength are less common for PAO modified bitumen than for SBS.

During thermo-oxidative aging of PAO-bitumen compounds, one generally observes a considerable decrease in penetration and a rise in viscosity, while the Ring and Ball value remains remarkably stable. These parameters usually evolve in the favorable direction.

Consequently, the most significant parameters to evaluate the long-term performance of PAO-bitumen compounds are those moving in the unfavorable sense; the cold flexibility, the quality of the dispersion and the macroscopic aspect. The quality of the dispersion and the cold flex of PAO-bitumen blends, in general, correlate well. The determination of the cold flex is in fact a traction at low speed. When the residual bitumen is not uniformly dispersed as small particles, but on the contrary appears in larger irregular agglomerates, these inhomogeneous regions create weak zones when mechanical stresses are applied. Thus being easily quantifiable, the cold flexibility is a very good indicator for the aging process. Nevertheless, to describe the aging performance more accurately, the more subjective microscopic and macroscopic observations are important as well.

To determine the aging conditions to be imposed, aging tests have been performed under different conditions (see Table 6): 4 weeks at 80°C (thermal); 6 months at 70°C (thermal); 2 years outdoor exposure and QUV aging. The QUV test is a widely accepted test to perform accelerated aging of bituminous roofing products under incident UV radiation in a standardized apparatus. All aging tests were executed on samples of finished PAO-bitumen membranes.

A first important conclusion of this parallel testing is that thermo-oxidative aging during 6 months at 70°C or during 4 weeks at 80°C appears more severe than QUV aging. The QUV test is often considered to be the equivalent of more than 10 years outdoor exposure. Furthermore, this implies that the influence of UV aging on PAO-bitumen compounds is relatively small compared to the combined influence of air and temperature. Moreover, the QUV test shows no difference for protected and unprotected PAO membranes. Another observation of interest is that the difference between thermo-oxidative aging during 4 weeks at 80°C and during 6 months at 70°C is not very pronounced. Running an appreciable number of aging tests on PAO-bitumen compounds, it was found that the variation of the cold flex with time during thermo-oxidative aging exhibits an asymptotic shape as illustrated in Figure 3.

Based on these results and data available,⁵ it can be concluded that a thermo-oxidative aging test during 4 weeks at 80°C is sufficiently severe to simulate real life performance

of PAO-bitumen in a reliable way, at least in normal situations. It is important to stress that this conclusion is not valid for SBS modified bitumen compounds. These systems do not age in a gradual and asymptotic way, but show an abrupt change in Ring and Ball and cold flex (see Table 7). It is practically impossible to predict when this drop will occur.

Experience in the field demonstrates that, in general, the performance of PAO-bitumen membranes is acceptable if the cold flex after 4 weeks of thermal aging at 80°C remains below 0°C without visual alteration of the surface. Moreover, the possibility to predict the change of the behavior of PAO modified bitumen by means of accelerated thermal aging has an important consequence. It permits to target PAO roofing, even with inferior characteristics, to specific environments in such a way as to obtain an excellent weathering performance.

FINAL CONCLUSIONS AND REMARKS

In order to ensure a long service life of PAO modified roofing membranes, it is imperative to consider the following points specifically related to the aging performance of the PAO-bitumen compound itself:

Crystallinity—An excessive content of the PAO-bitumen compound will inevitably lead to aging problems. Special attention must be paid to the fact that certain polymers, especially when mixed with bitumen, have a low crystallization rate. In this case, deterioration of the polymer-bitumen blend is only manifested after a longer period of time, while the initial properties were acceptable.

Molecular Weight—A positive correlation can be established between the molecular weight of the modifying PAO polymer and the resistance to aging of the resulting bitumen blend. The function of the high molecular weight is to better retain the absorbed bitumen constituents and to counteract the tendency of the residual bitumen particles to coagulate. To guarantee a good performance, it is advisable that 20 to 40 percent of added polymer is high in molecular weight. When different PAOs are combined, it is important to check the mutual compatibility.

Considering these guidelines when formulating PAO polymers with bitumen, it is possible to produce high quality roofing membranes with cold flexibility better than -20°C and with such a temperature susceptibility as to withstand weather conditions encountered in the major part of the livable world. Furthermore, it is possible to adapt the quality of the membranes to the specific needs encountered in waterproofing installations; in other words, to tailor the roofing to the real market application.

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REFERENCES

- ¹ Van Gooswilligen, G. and Vonk, W.C., "The role of bitumen in blends with thermoplastic rubbers for roofing applications," Roofing & Waterproofing Worldwide, VI International Conference, London, England, 1986.

- ² Lys, G. and Farges, C., "How to make bitumens compatible with SBS copolymers?" IVth Symposium of Eurobitume, Madrid, Spain, 1986.
- ³ Brûlé, B., Brion, Y. and Tanguy, A., "Paving asphalt polymer blends: relationships between composition, structure and properties," Proc. Association of Asphalt Paving Technologists, Vol. 57, pp. 41-64, 1988.
- ⁴ Petersen, J.C., "Chemical composition of asphalt as related to asphalt durability: state of the art," Transportation Research Record 999, TRB, National Research Council, Washington, D.C., pp. 13-30, 1984.
- ⁵ Schieroni, M. and Gagno, R., "La durabilit  della impermeabilizzazione delle opere idrauliche in terra e in calcestruzzo," Internationaler Abdichtungsverband, VII, Kongress, M nchen, (Paper), 1989.

FURTHER LITERATURE

- "Bitumen in de Weg-en waterbouw," H.E. Lubbers, NABIT edition 1985, Groningen, Holland.
- "Oxidation of bitumen in various tests," G. Van Gooswilligen, Eurobitume Symposium, The Hague 1985 (Paper).
- "Quantitative analysis of SBS and APP polymers in the modified bitumens," J. Wiertz, Eurobitume Symposium, The Hague 1985 (Paper).
- "Infrared spectrometry and broad chemical composition of bitumens during changes on road test section," J. Huet, Eurobitume Symposium, Madrid, 1989 (Paper).
- "Application of microscopic methods in the field of polymer-bitumen binders," C. Grimm, Eurobitume Symposium, Madrid, 1989 (Paper).
- "Bitumen analysis by thin layer chromatography (latroscan)," G. Leroy, Eurobitume Symposium, Madrid, 1989 (Paper).
- "Micromorphologie et propri t s m caniques d'un liant bitumineux SBS. Influence de la pr paration et due vieillissement," B. Br  l , RILEM Symposium, Belgrade, 1983 (Paper).
- "Investigations on physical-chemical properties of polymer-modified bitumen," J.P. Wortelboer, Internationaler Abdichtungsverband, VII. Kongress, M nchen, 1989 (Paper).
- "Comportement dans le temps des bitumes modifi s par des polym res," R. Degeimbre, Internationaler Abdichtungsverband, VII. Kongress, M nchen, 1989 (Paper).
- "Research work into modified bituminous binders with polymer additives," A. Dony, Eurobitume Symposium, Madrid, 1989.

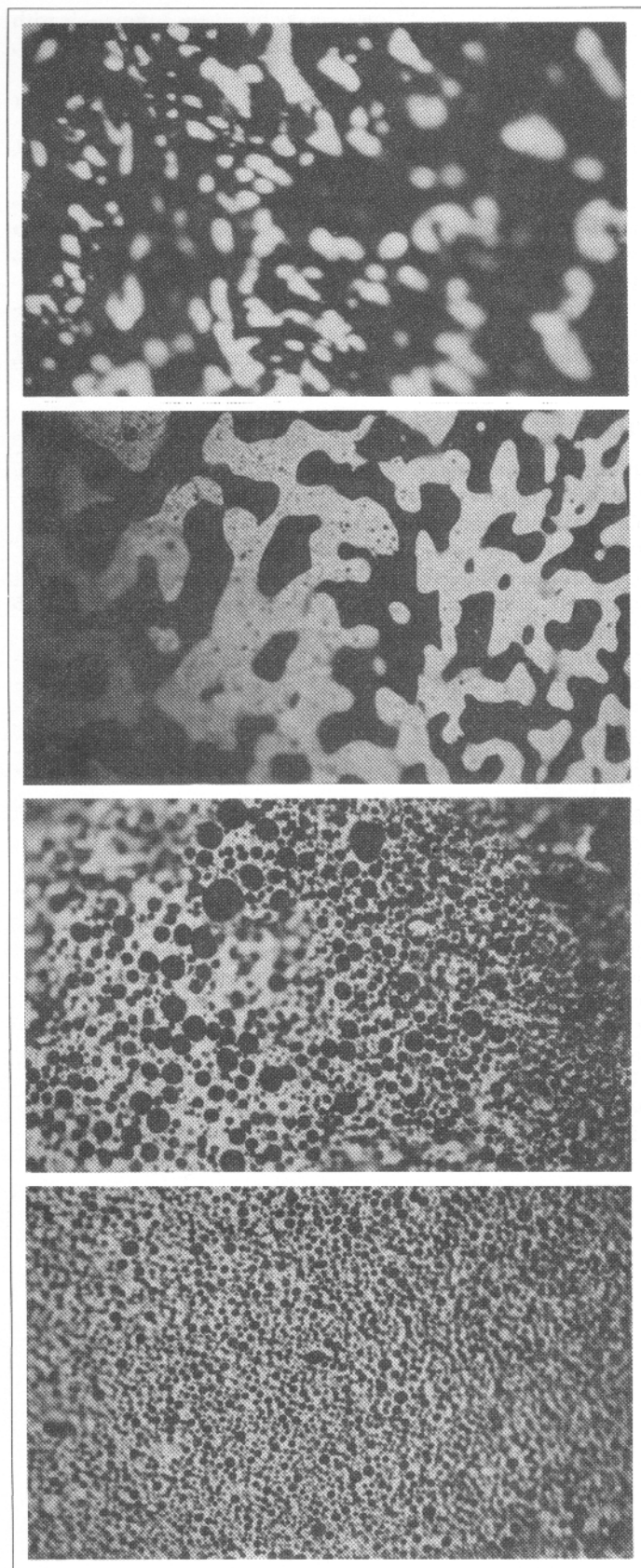


Figure 1 Evolution of the bitumen dispersion monitored by UV fluorescence microscopy (magnification: 100x, blend composition: 25 parts PAO/75 parts bitumen 190).

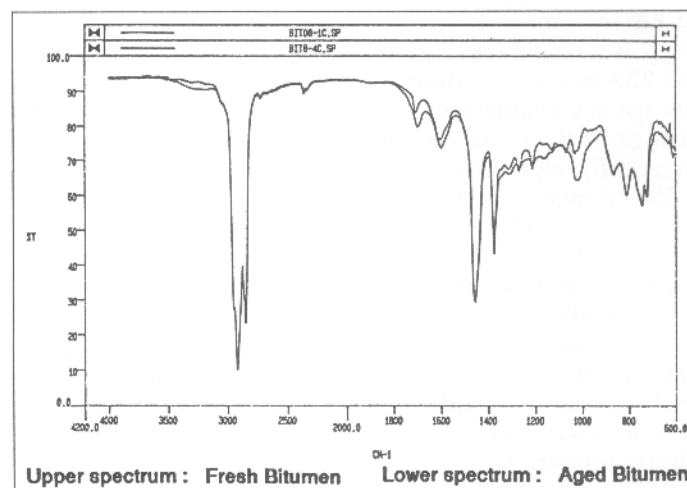


Figure 2 Infrared spectra of bitumen (pen. 190) before and after 4 weeks thermal aging at 80°C (air-circulated oven).

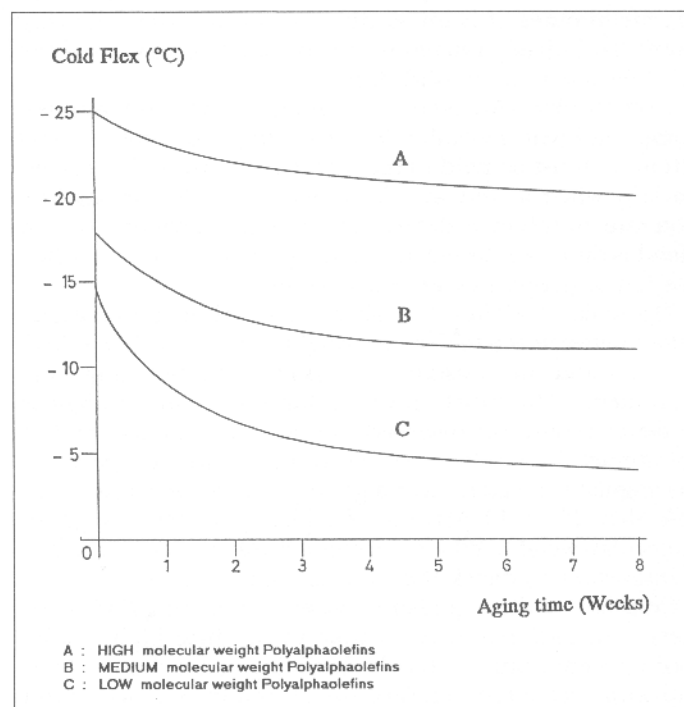


Figure 3 Evolution of the cold flexibility of PAO-bitumen compounds during thermo-oxidative aging (air-circulated oven 80°C, no UV). Generalized picture.

Bitumen 180-200 (parts)	100	84	82	0
PAO (parts)	0	16	18	100
Penetration at 25°C (dmm)	190	60	55	20
Ring and Ball (°C)	◀40	145	148	155
Cold Flex (°C)	▶0	-8	-18	-25
Microscopic aspect*		polymer embedded in bitumen	bitumen embedded in polymer	bitumen embedded in polymer

*By UV fluorescence microscopy

Table 1 Importance of continuous polymer matrix in a polymer-bitumen blend.

Polymer	Oil absorption capacity (%)	(*) percent polymer to obtain a continuous phase in bitumen (penetration 190)
SBS-1	500	6
PAO-1	200	18
PAO-2	150	22
PAO-3	100	24
(*): Polymer + bitumen = 100 percent (by weight) bitumen composition (see "Mechanism of Bitumen Modification with Polymers").		

Table 2 Correlation between oil absorption capacity of a polymer and its compatibility with bitumen.

Type	Initial	Thermal aging- 2 months at 80°C
PAO-1	-20	-20
PAO-2	-28	-24
PAO-3	-32	-28

Table 3 Polyalphaolefins - cold flexibility (°C) before and after aging of the pure polymer.

Blend Composition: 25 parts PAO/75 parts Bitumen (pen. 190)

Polymer crystallinity (%)	92	85	41	21
Cold flexibility (°C)				
Initial (fresh blend)	+ 5/P	0/P	- 10/P	- 22/P
2 weeks at 80°C	+ 10/B	+ 5/B	- 5/P	- 20/P
4 weeks at 80°C	+ 15/B(*)	+ 10/B(*)	0/B	- 20/P
P: Polymer builds continuous phase B: Bitumen builds continuous phase				
(*) Pronounced oil exudation and surface blistering				

Table 4 Effect of PAO crystallinity on thermal aging (80°C - air, no UV).

Surfacing Type	Initial	4 Wks. 80°C (thermal)	6 Mos. 70°C (thermal)	2 YEARS outdoor exposure*	QUV test
Mineral-Plain-	◀ - 15°C	- 10°C	◀ - 5°C	◀ - 10°C	- 10°C
Mineral-Plain-	◀ - 10°C	0°C	0/+ 5°C	- 10°C	- 5°C
Mineral-Plain-	◀ - 10°C			◀ - 5°C	- 5°C
Mineral-Plain-	◀ - 5°C	+ 10°C	+ 10/+ 15°C	0°C	+ 5°C

QUV: 4 cycles of 400 hours with alternating:
4 hours at 60°C - UV exposure
4 hours at 40°C - condensed water

Mineral: Membrane protected with mineral chippings.
Plain: Unprotected membrane.

(*) Site: Sona (VR), Northern Italy
Orientation: Southward
Application: Test rack, 1 in. thick plywood base
Inclination: 30 percent slope

Table 6 Change in cold flex of PAO-bitumen membranes in different aging tests.

Molecular Weight	High	Medium	Low
High PAO concentration (28 percent) - 1			
Cold Flexibility			
Initial (fresh blend)	-26/P	-24/P	-18/P
1 week at 80°C	-24/P	-22/P	-18/P
2 weeks at 80°C	-24/P	-22/P	-16/P
4 weeks at 80°C	-24/P	-22/P	-16/P
Low PAO concentration (20 percent) - 2			
Cold Flexibility			
Initial (fresh blend)	-20/P	-20/P	-14/P
1 week at 80°C	-20/P	-18/P	-10/P
2 weeks at 80°C	-18/P	-16/P	-7/B*
4 weeks at 80°C	-18/P	-16/P	-5/B*
1: 28 percent polymer with 72 percent bitumen (190 pen.) 2: 20 percent polymer with 80 percent bitumen (190 pen.)			
P: Polymer builds continuous phase B: Bitumen builds continuous phase			
(*) Alteration at the surface: oil exudation, blistering			

Table 5 Effect of PAO molecular weight on thermal aging (80°C - air, no UV).

Type	A	B
SBS	18	10
Bitumen 190	82	90
Cold Flex		
Initial	◀ - 25	◀ - 20
4 weeks 80°C	◀ - 20	◀ - 10
5 to 8 weeks 80°C	(*)	(*)
Ring and Ball		
Initial	120 · 125	120
4 weeks 80°C	110 · 115	105 · 110
5 to 8 weeks 80°C	100 · 105	95 · 100
(*) In some cases a sudden drop in cold flex to 0°C/ + 5°C was recorded after an aging period between 5 and 8 weeks.		

Table 7 SBS modified bitumen - thermal aging (80°C - air, no UV).