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# THE ROLE OF THE CHEMICAL INDUSTRY IN THE DEVELOPMENT OF ROAD TECHNOLOGY

DURING THE LAST FEW DECADES WE HAVE SEEN AN ACCELERATION IN THE INNOVATION OF ROAD TECHNIQUES. AN IMPORTANT ROLE IN THIS DEVELOPMENT WAS PLAYED BY CHEMISTRY AND THE CHEMICAL INDUSTRY. THE UNDERSTANDING OF BITUMEN CHEMISTRY HAS PERMITTED TO CHANGE AND IMPROVE BITUMEN STRUCTURE AND PERFORMANCE. THE INTRODUCTION OF BITUMEN EMULSIONS IS DUE TO A CHEMICAL APPROACH, BUT PROBABLY THE MOST EVIDENT CONTRIBUTION OF THE CHEMICAL INDUSTRY IS THE CREATION OF POLYMER MODIFIED BITUMEN; POLYMERIC MATERIALS ARE ALSO THE BINDER OF MOST COLORED PAVEMENTS. MORE RECENTLY, RECYCLING TECHNIQUES AND WARM ASPHALT MIXES HAVE BEEN INTRODUCED, MOSTLY BASED ON CHEMICAL ADDITIVES

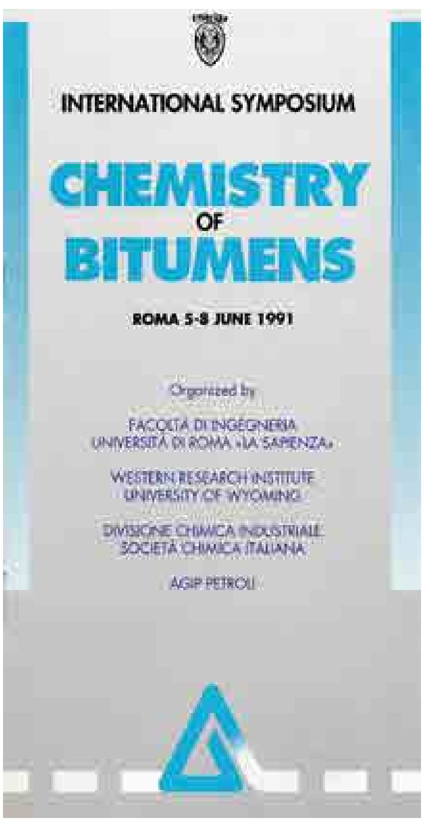


Fig. 1
The Symposium on Chemistry of Asphalt

In 1991 the first (and only) Symposium on the Chemistry of Asphalt was organized in Rome (Fig. 1). It was a success with a number of scientists from the USA in attendance, due to the recent conclusion of the SHRP program and the necessity to spread the information across Europe. Among them a Chinese gentleman: the famous T.F. Yen, inventor of the most important and famous model on bitumen constitution, based on the asphaltene dispersion in an oily phase [1] (Fig. 2). In spite of other models presented during the Symposium, with curious names such as *spaghetti and meat sauce* or the *swiss cheese model*, the Yen model is still the preferred model. Recent microscope analytical techniques such as the Scanning Electron Microscope (ESEM), confocal Laser Scanning Microscopy (CLSM) and mostly the Atomic Force Microscopy (AFM) have contributed to a deep insight into the bitumen structure and behavior (Fig. 3) and to the development of micromechanical models useful for the development of tailor-made chemical additives [2].

Since bitumen is a kind of *chemical soup*, obviously chemistry and the chemical industry have played an important role not only in its characterization, but also in developing technologies and additives for its use and improvement. Mostly in the last few decades we have seen an accelerated evolution in road technologies. Petroleum and Petrochemical Industries are involved in such processes, besides the fine-chemical Companies specialized in additive production. Let us review some of the chemical innovations related to road technology.

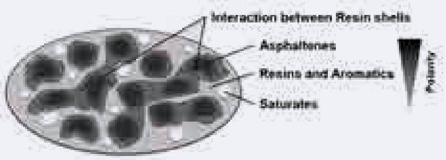


Fig. 2
Bitumen microstructure

Fig. 3
AFM analysis of bitumen showing micelles made of asphaltene core (bees) with a shell of highly polar resins

## Changing the bitumen chemical structure

Probably one of the first interactions between chemistry and bitumen was the oxidation (air blowing) process created to upgrade soft residues or bitumens to products with superior viscoelastic properties. The main effect of air blowing is a dehydrogenation that converts some of the relatively low molecular weight *maltenes (resins and oils)* into *asphaltenes*. The result is an increase in the softening point and a lower temperature susceptibility, especially useful for waterproofing applications. The same result can be obtained by adding sulfur to a heated bitumen, with the evolution of $H_2S$ (Fig. 4) [3]; in fact, the petroleum refining industry has long tried to add the byproduct sulfur to road bitumen, without success. Two kinds of catalysts were mostly used to produce air blown bitumens: iron trichloride (mostly) and phosphorous pentoxide. The first one is the most effective [4], while $P_2O_5$ is not a true catalyst but influences the bitumen structure. In fact, it has been discovered that the addition of phosphoric and polyphosphoric acid induced into bitumen a shift from sol to a more gel-like structure, similar to that generated by air blowing, but with a minor influence on low temperature properties [5-7]; the Tgδ *vs* T plots provide useful information on bitumen colloidal state and on its viscoelastic behavior (Fig. 5) [8]. The chemical industry has since then provided a number of phosphorous additives that increase the ageing resistance and other properties of bituminous binders. Moreover, the compatibility with polymers is greatly improved because the bitumen ability to blend with some polymers changes with its colloidal state [9].

## The revolution of polymer modified bitumen

The major involvement of the chemical industry in road technology was driven by the introduction of polymer modified bitumen (PMB). The *marriage* of bitumen with polymers is not an easy one: different densities, different viscosities, no chemical affinity made the creation of a homogeneous stable mixture difficult [10].

The use of crumb rubber from worn-out tires can be considered a precursor of PMB in the U.S., with the indirect involvement of another chemical industry, the rubber and tire producers. Another precursor is surely the prolypropylene (PP) petrochemical industry in Italy at the end of the fifties: the first isotactic-PP processes produced an appreciable amount of a waxy, low-molecular weight by-product (*atactic* PP). that was a waste material. Following a brilliant idea, it was mixed with bitumen (14-20% PP by weight) to produce waterproofing membranes, thus creating a flourishing business.

However, the development of the actual PMBs came together with the invention of porous asphalt (Fig. 6), that needed a superior, strong binder with elastomeric properties. The chemical industry proposed a number of

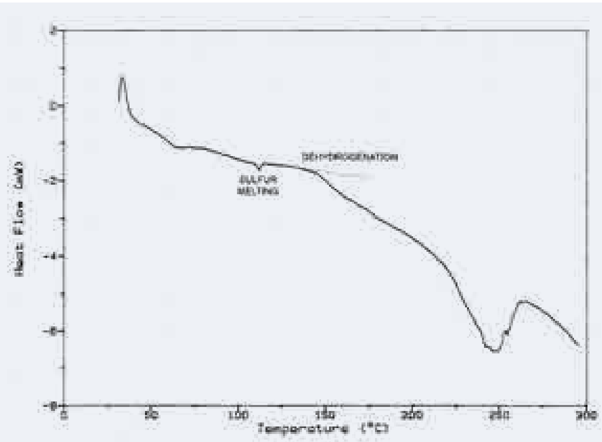


Fig. 4

DCS heating curve of bitumen plus 4% sulfur, in the presence of air: the bitumen dehydrogenation reaction (with $H_2S$ evolution) starts after the melting of sulfur at about 145 °C

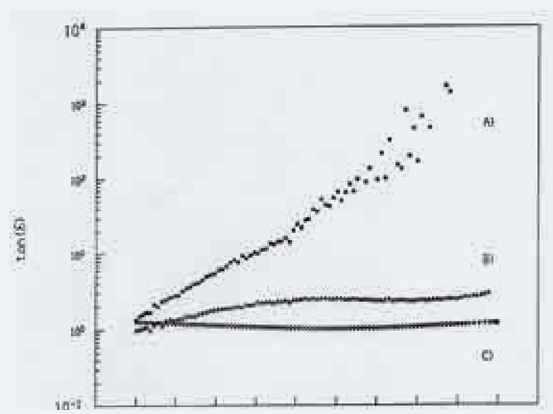


Fig. 5

Rheometric curves of a SR bitumen (A), and of the same bitumen blown (C) and treated with 3% $(HPO_3)_n$ (sample B). The curves of the oxidized and acid-treated bitumen are similar

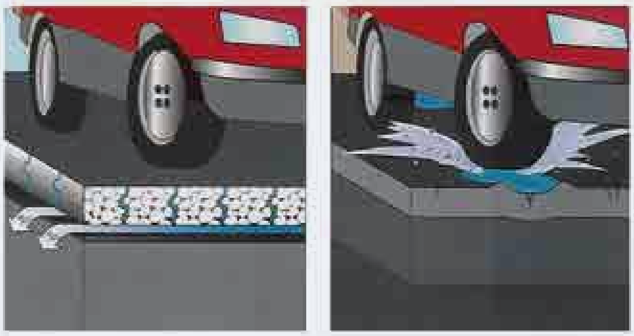

Fig. 6

Working principle of porous asphalt

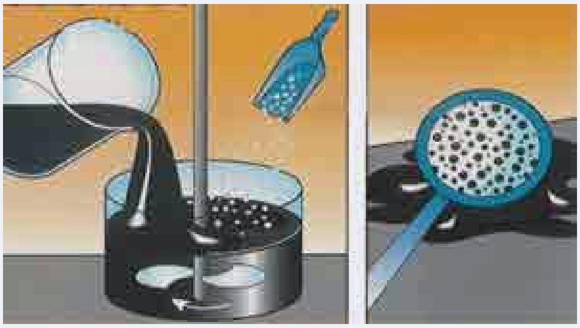

Fig. 7

Small percentages of a suitable polymer create a polymeric continuous phase including the bitumen particles

polymers: EVA EMA, SBR, SBS, SIS, EPDM [11]. The problem was the compatibility and stability of the mixture; an effective polymer had to be capable of creating a continuous phase, absorbing (incorporating) the bitumen particles (Fig. 7), also when used in small quantities (4-6%). SBS, a thermo-elastomeric polymer, has since then become the most popular, producing relatively stable mixtures. Polymeric systems crosslinking inside the bitumen structure have been also proposed. PMBs are today widely used in porous pavements (for water drainage and noise reduction) and also in high-modulus asphalt. The recent studies on *perpetual pavements* and on *thinlys* are frequently based on PMBs, which are probably the most important innovation of the last century in asphalt pavement technology.

## Polymers on the road

After about a hundred years of use, bitumen was tired of being considered a black material and tried to turn white by taking away the asphaltene skeleton, responsible for the black color. The result was a binder that was too weak; the only way to produce a colorless binder was, therefore, to ask the chemical industry for help again. In fact, actual colorless or brightly-colored *asphalt* is totally or almost totally made by using polymeric binders, having workability and behavior similar to that of the bitumen (Fig. 8). The choice of a cheap synthetic material, competing with bitumen, is not an easy task and research is underway to solve the problem. The so-called hydrocarbon resins, a cheap tacky byproduct of the steam cracking process have been used with EVA; other polymeric systems are in use (e.g. acrylic polymers).

With the help of colored aggregates and of chemical additives, such as iron oxide, bitumen can still be used as a binder for dark-colored pavements (e.g. deep red and green). Moreover, the chemical industry produces a series of pigmented slurry surfaces in a range of colors; applied in very thin layers, they are suitable for pedestrian and

Fig. 8

A colored road

Fig. 9

The recycling process of the road pavement

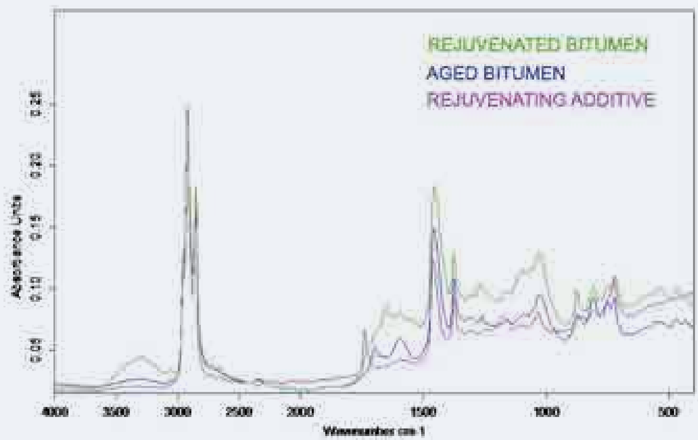


Fig. 10

Superimposed FTIR spectra of an old (oxidized) bitumen, of a rejuvenating additive and of the rejuvenated bitumen

lightly trafficked areas. Thermoplastic and thermosetting materials are used (acrylic, epoxy, polyurethane etc.) (Fig. 9).

### Cold and warm techniques need chemistry

Oily and greasy substances are not water soluble; chemists found the way to finely disperse them into a stable oil-water system, that is emulsion: bitumen emulsions were thus created. The first patent by an English chemist (Alan Mackay) is dated 1922; however, bitumen emulsions became popular in the second half of the last century, especially after the first petroleum crisis (1973), with the development of the so called *cold road techniques* [12]; the use of emulsion greatly reduced fume emission and fuel consumption. In order to create an emulsion, besides a strong stirring action, it is essential to use a chemical called emulsifier, that helps to disperse the small bitumen droplets into the water phase. The emulsifier is the single most important constituent of any bitumen-in-water emulsion. The literature on emulsifiers is very large and many chemical industries produce them; the traditional types based on amines, quaternary ammonium compounds, amidoamines, alkoxylated amines (*cationic emulsions*) and fatty acids or sulphonate products (*anionic emulsions*) are now evolved to various formulations, many of them based on natural, non-toxic products. The use of bitumen emulsion as tack coat, adhesive, surface treatments, cold asphalt mixes, recycling agent, is well known. In a number of such applications the use of polymer modified emulsions is common, that is an upgrading of the cold technology, following the wide use of PMBs in road works.

In the last two decades another approach was used to reduce fumes and energy in road making, with the introduction of the so-called *warm techniques*. Again the chemical industry played an important role proposing the use of special additives capable of lowering the viscosity of the binder and, therefore, the temperature of the traditional asphalt mix, from about 150-160 °C down to about 120 °C or less. Sasol waxes from the Fischer-Tropsch process (melting in the range 110-130 °C), are added to the bitumen to improve workability in that range. The addition of chemical zeolites lowers the paving temperature through another mechanism: the evolution of water vapor during heating, that acts as a foaming-fluidizing agent on the binder.

### Adhesion agents

Typically, the adhesion of bitumen to aggregate is not a problem; however, in the presence of water, unexpected adhesion-related problems may occur. Hydrated lime (1-3% as part of the filler content), which reacts with the bitumen carboxylic acids, has traditionally been used as an anti-stripping agent. The electro-chemical balance forces the water away from the aggregate. Since then a number of chemical additives have been developed to improve adhesion, generally based on amines (especially fatty polyamines) and amine derivatives such as amides, etc.; the first papers of interest appeared in the forties, but the extended use of such additives started in the 1960's and 1970's of the last century. It is believed that the amino groups are attracted to the aggregate surface, whilst the fatty groups remain in the bitumen; the interfacial tension is lowered. The percentage of additive varies generally between 0.3 and 0.6% on the binder.

It was probably the spreading of the anti-stripping products that prompted the development of a number of small and medium size industries specialized in their development and marketing, followed by the creation of other kinds of additives for asphalt mix and road works.

### Asphalt recycling

Asphalt pavement recycling is now a common practice and can be carried out in situ or in a different way, by using hot, cold or warm techniques. The main mechanisms for the ageing of bitumen are oxidation, loss of volatiles, and molecular rearrangement; oxygen incorporation increases the polarity, allowing the formation of molecular associations. Polar aromatics and the higher molecular size fractions are converted to asphaltenes, and this hardens the bitumen. Therefore, aged bitumen contains excess asphaltenes and is depleted in polar components. The addition of fresh asphalt hot mix to re-establish aggregate gradation as well as to soften the old material, is not sufficient to restore the original characteristics of the bitumen.

Again, chemistry is helping with rejuvenating agents, largely consisting of lighter polar fractions capable of restoring the compositional balance of the recycled material. Generally, the addition of aromatics decreases the tendencies toward hardening. Commercial additives are proprietary and the composition is variable; traditionally they contain a dispersant-solvent base and a polar component, normally containing nitrogen groups, which also act as adhesion agents.

Owing to the complexity of the bitumen structure and to the small amount of added additive, it is not easy to detect any chemical reaction and formation of new chemical compounds, in spite of differences observed in FTIR spectra (Fig. 10). Without doubt, the additive interacts at an electronic and molecular level, by *disturbing* the molecular associations formed during ageing and creating new aggregations. Its action is more connected to the formation of secondary

links than to the creation of main links. The formations of molecular associations are the result of ageing and hardening: their total or partial elimination results in a *rejuvenated*, less viscous and more performing binder.
New recycling practices have introduced PMB use and the application of warm techniques, so adding more *chemical value* to the recycling practice.

### Chemistry for potholes

Over recent years, severe winter weather and lack of maintenance has caused significant damage to local road networks. This has manifested itself in a significant increase in the number of potholes. Potholes are one of the main local concerns, as they are highly visible defects, and the selection of the right treatment is potentially complex. The traditional cold mixes applied as a reactive maintenance are not effective; hot rolled asphalt is better, but not practical or economical to be quickly applied in many small sites.
Over the last years, the road sector has moved towards special mixtures that can be applied at room temperature and, sometimes, in wet conditions. They can contain RAP (recycled asphalt pavement) and special additives. The help is again given by chemistry, in the form of organic compositions or semi-polymeric additives capable of hardening and rapidly creating a solid and flexible mixture (e.g. polyurethane or silylated urethane prepolymers). Of course they are proprietary materials and the user does not know the exact composition, but only their performance, which is normally sensitive to an appropriate use and to laying conditions.

### Anti-ice and poly-function additives

Chemicals, usually in the form of salts, are normally spread in winter on the roads to avoid ice formation. Now the chemical industry produces special additives to be added directly to the asphalt mix; they are, therefore, directly incorporated into the road pavement and delay ice formation. They are not necessarily based on inorganic salts; compounds such as urea, polyethylene glycol or other organic materials can be used.
The increased demand for high performance and durable asphalt mixes has prompted the development of various additives and new mixes. Chemical-structural modification can be achieved by adding directly at the asphalt mixing plant poly-function materials capable of influencing more properties in the mix, such as modulus, adhesion, temperature, durability etc. They can contain polymers, fibers, waxes, anti-stripping agents etc. and can be tailor-made for a specific application.

### Conclusions

Bitumen is a very complex material: chemistry and chemical industry have played an important role in its characterization and in developing technologies and additives for its use and upgrading.
In the last few years we have seen an accelerated evolution in road techniques. Petroleum and Petrochemical industries are involved in such process, besides the Fine Chemical Companies specialized in additive production. Their contribution will probably become more important in the future.

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**Il ruolo dell'industria chimica nello sviluppo della tecnologia stradale**

Durante le ultime decadi abbiamo assistito a un'accelerazione nell'innovazione delle tecnologie stradali. Un ruolo importante in questo sviluppo è dovuto alla chimica e all'industria chimica. La comprensione della chimica del bitume ha permesso di cambiare e migliorare la struttura e le prestazioni del bitume. Una vera rivoluzione è stata l'introduzione del bitume modificato con polimeri o addirittura la sua sostituzione con resine sintetiche. La chimica è poi entrata nei processi di riciclaggio, nelle tecnologie per ridurre le temperature e per migliorare l'adesione, ma anche per chiudere… le buche.



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