POLYPROPYLENE - ASPHALT MIXTURES
FOR WATERPROOFING MEMBRANES

Paolo Italia, Ernesto Brandolese
Production process and modified asphalt project leaders
EURON S.p.A. (Research Company of AGIPPETROLI - ENI Group)
Via F. Maritano 26 - 20097 S. Donato Milanese (MI)
Italy

Abstract
In any field of polymer-asphalt mixtures application is estremely important to achieve a very good compatibility between the components in order to improve as much as possible the performances due to the polymer content.
In the case of waterproofing membranes application this compatibility reduce, moreover, the amount of polymer required to obtain the best performances.
Using the Colloidal Instability Index Ic, as measured by the Iatroscan device, we propose a correlation between asphalt's chemical characteristics and the polymer minimum amount sufficient to disperse in a stable way the asphalt itself in the polymeric matrix.
As a result, through the proposed correlation, with a simple asphalt composition analysis it is possible to predict its performance when mixed with polypropilene.
In the paper, beside the description of the Iatroscan analytical technique, we also present a method for determining phase inversion based on optical fluorescence microscopy performed on about 30 different samples of asphalt.
We also present the experimental correlation laws between the polymer amount at phase inversion and the asphalt single components content.

1 - Introduction
As a waterproofing material, the asphalt can be used in the industrial field in many different ways: it can be found in finished products such as waterproofing membranes, paints, pastes, mastics and oxidated asphalts.
In Europe, the waterproofing membranes are the most important market; according to the modern manifacture processes these membranes consist of a rigid support (for instance, polyester) impregnated with a mixture of asphalt, polymer and mineral filler.
Each company has its products and its processes and tries to minimize the polymer content (the most expensive material), maintaining at the same time some essential requirements as cold flexibility, thermal stability, and resistance to degradation caused by the atmospheric agents.
It is therefore very important the research for asphalts with good characteristics of compatibility with the polymers in use (mostly atactic polypropylene, a refuse of the isotactic polypropylene, or similar products); compatibility is the capability of the asphalt to combine homogeneously with the polymer, in order to achieve a morphologic structure in which the polymer prevails.
As a matter of fact, even if the mixture consists mostly of asphalt, the so-called reverse phase of the mixture can be achieved with the right quantity of polymer: in fact, the polymer incorporates the particles of asphalt. Only when the polymer prevails the characteristics of elasticity and resistance reach their maximum.

### 2 - Preparation and valutation of the asphalt/polymer mixtures
In the polymer-asphalt tests carried out in the Asphalt Laboratory of EURON, research company of AGIPPETROLI for energy sector, was used a propylene-base product, having the following characteristics:

| melt viscosity at 190°C	mPas	100.000
softening point R. and B.	°C	>150
needle penetration	dmm	20
density at 23°C	g/cm3	0,9
viscosity number "J"	cm3/g	100
molecular weight	Mv	85.000
intrinsic viscosity	g/100ml	1,0
glass transition temperature	°C	<-30

The additivation was carried out according to the following procedure, starting with 200g of mixture at 10% of polymer and adding 2g of polymer each time:

- preheat the asphalt in a nitrogen flow at a maximum temperature of 120°C, in order to transfer 180g in a 250g can. Heat in a thermostated bath at 185°C with air and mix for 15 minutes with a slanted-pallet stirrer, at a speed of 600 rpm;
- add 20g of polymer (10% in the mixture) in small doses, stirring it for 60 minutes, at a constant temperature of 185°C;
- take two drops of the mixture with a glass rod and place them on a slide; these drops must be at once cooled in distilled water, and then dried with a compressed air flow;
- observe then with a fluorescence microscope: observe at least three areas in order to remark possible cases of dishomogeneity (take a small part of the second drop in order to verify the reverse phase even in the sample). Two characteristics must be found in order to ascertain the reverse phase: the continuous polymer phase (white field) with small black drops representing the discontinuous asphalt phase, and the homogeneous scattering of the small drops (see the following pictures);
- if there is no reverse phase, add 2g more of polymer (about 1% more than the previous mixture), and, after stirring for 30 minutes at the constant temperature of 185°C, observe with the fluorescence microscope according to the previous procedure. The test continues according to the procedure until the reverse phase is determined.

In the following pictures it's possible observe no reverse phase (13% of polymer) and reverse phase (16% of polymer) for sample number 9.
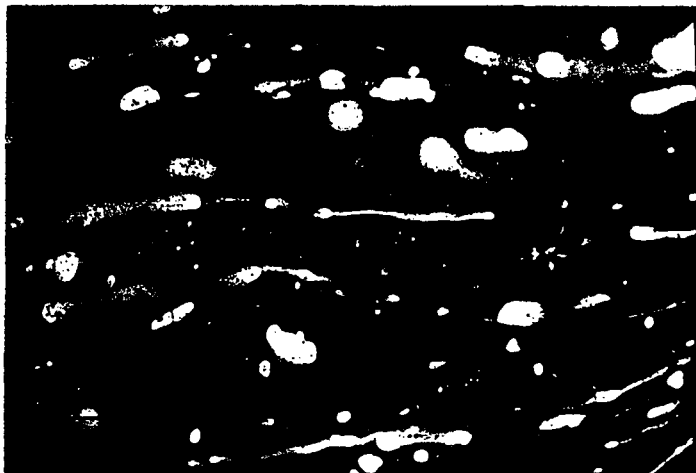
Sample number 9, 13% of polymer: no reverse phase
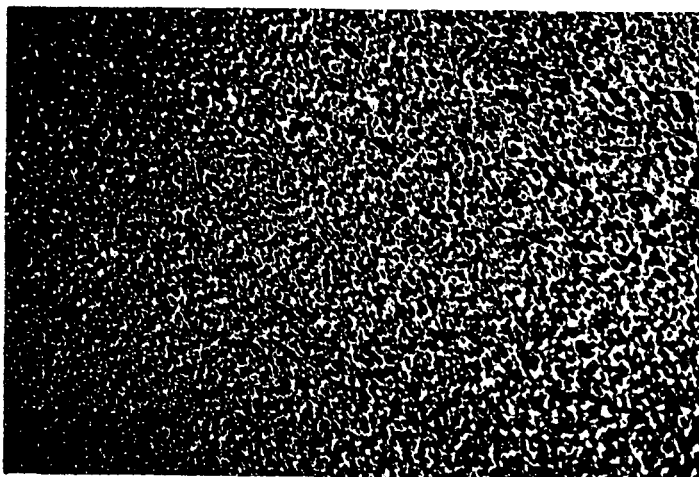
Sample number 9, 16% of polymer: reverse phase

3 - Asphalts characteristics

For each asphalt used in the previous mixtures (27 samples), was determined the usual characteristics and the Colloidal Instability Index with the thin layer chromatographer Iatroscan. The index is the ratio between asphaltenes + saturated and resins + aromatic compounds.

The Iatroscan analysis (mod. MK-5) is a thin layer chromatography (TLC) connected to a patented Flame Ionization Detector, similar to the FID used in gaschromatography. The main difference between the usual TLC and the Iatroscan analysis is that the plate is substituted by a frame consisting of ten small quartz bars, covered by a thin layer of silicon dioxide or sintered alumina, applied with a special technique.

At the end of each bar place with a microsyringe a microliter of the solution at 1% of asphalt in dichloromethane; after completing the frame, put it under elution with solvents in a series of three spot resolution chambers for TLC. After each resolution, eliminate the eluent through stove evaporation. Using the stationary phase of the silicon dioxide and the action of the mobile phase, it is possible to separate the substances according to the degree of polarity and similarity to the solvent. For the asphalts, start with the normal-hexane in order to separate the satured compounds, then use a mixture toluene/normal-hexane for the aromatic compounds, and finish with a mixture of dichloromethane/methanol for the resins which have strong polar characteristics. All that remains on the glass rod is asphaltene.

At the end of the resolution phases, the frame must be placed in an appropriate part of the instrument; here the small bars keep on passing between the two poles of the detector for all its length at constant speed; the process is fully automatic. The organic substances which have been separated on the thin layer are therefore ionizated by the flame and their quantity can be measured. The instrument software makes also possible the data elaboration and the calculation of the per cent composition of the mixture using the method of the normalization of the peak area.

In the following tables the characteristics of the asphalts used in this experimentation are reported together with the chemical composition, the Colloidal Instability Index and the polymer amount necessary to achieve the reverse phase according to the previously described procedure.

sample number		1	2	3	4	5	6	7	8	9
penetration	dmm	257	254	190	194	182	193	185	217	190
softening point R. B.	°C	40.5	41	42.5	39	42	38.5	38.5	39	43
asphaltenes	%wt.	27.4	25.4	20.7	24.1	28.4	23.7	24.5	25.4	25.0
satured	%wt.	8.8	8.9	3.6	2.4	4.2	6.6	3.4	4.2	5.3
resins	%wt.	25.8	27.8	18.7	24.5	21.9	28.3	33.1	30.8	34.3
aromatics	%wt.	38.0	37.9	57.0	49.0	45.5	41.4	39.0	39.6	35.4
index Ic	-	0.57	0.52	0.32	0.36	0.48	0.43	0.39	0.42	0.43
polymer	%wt.	11	13	20	18	14	16	17	16	16

sample number		10	11	12	13	14	15	16	17	18
penetration	dmm	175	172	167	190	165	206	174	155	134
softening point R. B.	°C	40.5	42	45	39	43	39	42	45	43
asphaltenes	%wt.	21.1	25.2	25.5	24.7	23.8	14.8	25.0	28.3	21.6
satured	%wt.	4.1	4.4	2.2	3.6	4.8	4.0	4.7	5.3	3.8
resins	%wt.	37.2	40.1	23.6	33.5	22.2	23.3	18.8	24.1	22.8
aromatics	%wt.	37.6	30.3	48.7	38.2	49.2	57.9	51.5	42.3	51.8
index Ic	-	0.34	0.42	0.38	0.39	0.40	0.23	0.42	0.51	0.34
polymer	%wt.	18	16	18	16	16	24	16	14	22

sample number		19	20	21	22	23	24	25	26	27
penetration	dmm	165	245	168	190	205	155	163	199	190
softening point R. B.	°C	45.5	36	40.5	39	37.5	45	42.5	41	42
asphaltenes	%wt.	28.0	23.2	19.8	19.0	24.9	19.4	21.7	31.9	17.8
satured	%wt.	7.3	4.7	3.6	7.1	3.7	5.3	4.7	6.3	2.7
resins	%wt.	26.2	19.9	23.2	18.6	21.1	24.5	24.2	22.3	16.8
aromatics	%wt.	38.5	52.2	53.4	55.3	50.3	50.8	49.4	39.5	62.7
index Ic	-	0.55	0.39	0.31	0.35	0.40	0.33	0.36	0.62	0.26
polymer	%wt.	13	17	21	18	16	19	18	10	22

4 - Conclusions

Averaging the previously reported data, for each polymer amount at the reverse phase used in the present work, an optimum distribution of the four main asphalt's components has been calculated and related to the Colloidal Instability Index Ic.

content of polymer		10%	11%	13%	14%	16%	17%
asphaltenes	%wt.	31.9	27.4	26.7	28.3	24.6	23.2
satured	%wt.	6.3	8.8	8.1	4.8	4.8	4.7
resins	%wt.	22.3	25.8	27.0	23.0	28.0	19.9
aromatics	%wt.	39.5	38.0	38.2	43.9	42.6	52.2
index Ic	-	0.62	0.57	0.53	0.49	0.42	0.39

content of polymer		18%	19%	20%	21%	22%	24%
asphaltenes	%wt.	22.9	19.4	20.7	19.8	19.7	14.8
satured	%wt.	3.2	5.3	3.6	3.6	3.2	3.9
resins	%wt.	23.9	24.5	18.8	23.2	19.8	23.4
aromatics	%wt.	50.0	50.8	56.9	53.4	57.3	57.9
index Ic	-	0.35	0.33	0.32	0.31	0.30	0.23

From figures of the previous table, it could be concluded that:

1) A poor compatibility is mainly related to an high aromatic and low saturated and asphaltenes content.
   In fact, in the interval of polymer content at the phase inversion from 10 to 24%, we observe a 50% of aromatic increment and a 50% of saturated compounds and asphaltenes decrement, while resins change only about 10%.
2) Only asphalts having an Ic > 0.5 (more then 1/3 of asphaltenes + saturated compounds and less then 2/3 of resins + aromatic compounds) give high polimer compatibility, with reverse phase from 10 to 13% of polymer.

In the next figures it is possible to obtain the trend of the polymer content at the reverse phase as a function of colloidal instability index Ic and as a function of asphaltenes, saturated components, resins and aromatics.
According to the values reported in the Figure 1, it is possible to define the following law of correlation between the polymer amount at the reverse phase and the colloidal instability index:

$$\boxed{\% \text{ polymer } = 33.9 - 41.7 \text{ x Ic}}$$

Using this correlation is further possible to calculate the polymer amount at reverse phase for each asphalt type avoiding to prepare and evaluate various experimental mixture.

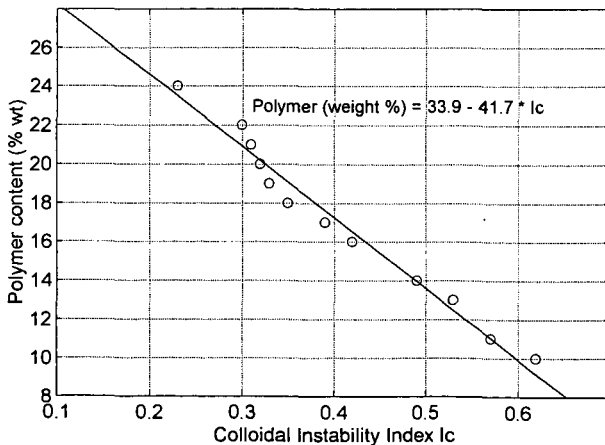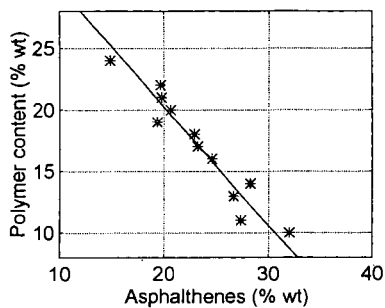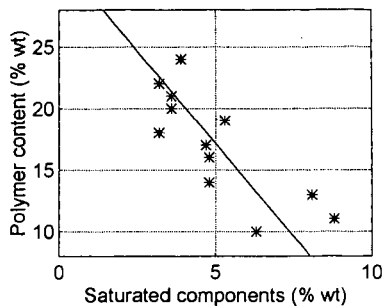### Figure 1

Polymer (weight %) = 33.9 - 41.7 * Ic

Colloidal Instability Index Ic

Figure 2

Figure 3

Figure 4

Figure 5