EVALUATION OF EMISSIONS PRODUCED FROM THE MODIFICATION OF BITUMEN WITH SBS AND GRANULATED RUBBER

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ABSTRACT

Conventional bitumens, used in most of the roads, unfortunately do not reflect a satisfactory performance. In particular problems such as permanent deformation of asphalt pavements, stresses, and cracking, deterioration of roads, resulting from the increasing number of vehicles, traffic loads and seasonal effects, are most frequently encountered problems.

Adding various additives into the bitumen to eliminate distortions in order to improve performance has become now a common practice. The most commonly used additives are SBS polymers and granulated rubber. However, these additives are stirred in a facility at a minimum of 180° degrees with bitumen and a binder is obtained to be used in hot asphalt mixtures.

In the extend of this study, the emission values of the exhaust gas, occurred during the production process at the facility, where the modification of the penetration class bitumen has been carried out at high temperatures with SBS polymer and granulated rubber, has been compared with the rates given in the Air Pollution Control Regulation and the results has been evaluated.

Keywords: Emission, Modifier, Rubber, SBS, Polymer

1. INTRODUCTION

As a result of recent challenges in the world, like "Global Climate Change and Carbon Footprint", all industries should take into consideration the current trends, mainly addressing the "sustainability". The European Commission (EC) has given special importance to this issue by publishing several directives focused on "Sustainable and efficient use of natural resources, energy and materials". The EC Action Plans fully take into account competitiveness, energy, environmental and social aspects. The aim is to improve the way materials are produced, design of the products coming to the markets and the way they are consumed.

According to two of EC themes and policies, the asphalt industry should concentrate on " The use of materials/ re-use / recycling / efficient construction" and "Minimizing waste". However, in the industry policy [1] , the conditions for using stream of waste in the production of asphalt mixes are mentioned as follows and asphalt industry should make sure addressing those issues when using the secondary materials (like glass, rubber; etc) during asphalt production.

Waste streams from other industries are only used if there are:

- No adverse effects on the health and safety of workers in the industry
- No environmental impacts- instant or in the future
- Future recyclability and the potential of reuse of asphalt remains
- No negative impact on the technical performance of the product

It is well known that, in time, some deterioration occur on the road surface such as rutting, fatigue and cracking. The use of crack repair materials, to repair road cracks which occur for reasons such as careless and incorrect applications, temperature changes, excessive axle loads and repetition of these forces, is of great importance for extending the life of the pavements by preventing the distortions on surface, reducing of the maintenance and repair costs, and improving the safety and comfort of driving. The application of these materials can be performed in "sealing "or "filling "fashion if the crack width is between 3-20 mm. Should the crack width be over 20 mm, "mortar type coating" or "fine grained bituminous hot mix materials" are used to fill the cracks. Applications can be cold (Bituminous emulsion or Polymer bitumen emulsion) or hot (bitumen, fiberized asphalt, rubberized bitumen, rubberized asphalt, low-modulus rubberized asphalt, chemically cured thermosetting materials, self-leveling silicones) Some additives/polymers can also be added to the binders in the production of these materials.

In this study, we have produced calcite added SBS modified bitumen and 2 different binders containing "granulated rubber" material in order to obtain bituminous materials with higher elastic recovery which would; fill the crack width better; not flow freely inside the crack; increase the softening point over 100°C; and increase the dynamic sheer rheometer co-efficient. The rates of additives in the binders are %8-10 SBS; %8-12 calcite and as alternative % 5-10 granulated rubber.

The ever increasing problem of air pollution, especially problematic in residential areas where the industry is dense, is affecting our lives negatively and creating very serious health problems. The effect of the industrial facilities, being one of the sources of air pollution, is approximately 20%. Choice of wrong location, not taking precautions necessary for the protection of environment, using low quality fuels in the burners and not utilizing appropriate technologies are known to be the main reasons causing air pollution.[2]

In this study two different crack sealing materials, to be used in rehabilitation of the cracks occurred in the pavements, are produced (by adding granulated rubber to the calcite added SBS modified bitumen) at ISFALT A.Ş. -HABIBLER ASPHALT FACTORY, Cebeci District Istanbul –Turkey, using a natural gas operated modified bitumen production facility with a capacity of 12 tones/hour .

The VOC (Volatile Organic Compounds) and dust measurement values are gathered through the ventilation shaft of this modified bitumen production facility, in order to compare emissions released by rubber- as a secondary material in pavement applications- modification process, against the SBS modification mixes, and the results later are compared to the current limit values of the air quality protection regulations governing country's industrial compounds' emission rates.

2 .MATERIALS USED IN THE PRODUCTION OF MODIFIED BITUMEN

2.1 Bitumen B50/70

Bitumen from the Izmit Refinery of Turkish Petroleum Refineries Inc. (TÜPRAŞ) has been used in the production as bitumen with the penetration class B50/70. The characteristic of the applied bitumen is given in Table 1.

Table 1: Conventional Binder Test Results and Specification

Properties	Unit	Test Method	Test result	B 50/70 Specification TS EN 12591
Penetration	0.1mm	TS EN 1426	55.0	50 - 70
Softening point	ºC	TS EN 1427	49	46 - 54
Fraass Breaking point	ºC	TS EN 12593	-8	Max., -8
Flash point	ºC	TS EN 2592	332	Min., 230
Specific gravity	g/cm^3	TS EN 15326	1.021	-
Loss on heating (TFOT)	%	TS EN 12607-2	0.4	Max., 0.5

2.2 SBS (Styrene-Butadiene-Styrene) Polymer

Styrene-Butadiene-Styrene Block Co-polymer, shortly SBS, has been used in the bitumen modification. The characteristics of the SBS modified bitumen is given in Table 2.

Table 2: Bitumen characteristics with SBS Co-polymer modified

Properties	Unit	Test Method	Test result
Penetration	0.1mm	TS EN 1426	41
Softening point	ºC	TS EN 1427	78
Flash point	ºC	TS EN 2592	310
Elastic Recovery	%	TS EN 13398	97
DSR (Pass fail temperature)	ºC	TS EN 14770	80
RTFOT	%	TS EN 12607-1	0.1

2.3 Calcite

Calcite , with the chemical formula of CaC03, which is required as a filling material in order to use the manufactured modified bitumen in sealing and filling of cracks on roads, has been obtained from Eskisehir region.
The characteristics of the Calcite used are given in Table 3 according to the chemical analysis, carried out by the Turkish Scientific and Technological Research Institution Marmara Research Center (TUBİTAK MAM).

Table 3. Calcite Dust XRF results

Compound	Amount %
Al203	0.407
BaO	0.082
CaO	81.628
Cl	0.030
Fe203	0.114
MgO	17.110
P2O5	0.109
SO3	0.036
Si02	0.454
SrO	0.030

2.4. Granulated Rubber

Granulated rubber, used in the research, has been supplied by a company in Ankara. The characteristics of the granulated rubber, between 0-0,5mm, are given in Table 4 according to the chemical analysis, carried out by TUBİTAK MAM Material Institute.

Table 4: Granulated rubber chemical analysis

Softener (TEEM)*	% 6 83
Amount of rubber	% 52.91
Amount of carbon black	% 29.30
Amount of inorganic materials	% 10.97
Type of rubber	Natural rubber/ SBR mixture

*TEEM. Total material which can be extracted- process facilitator materials, plasticizers and latex without cross link was found.

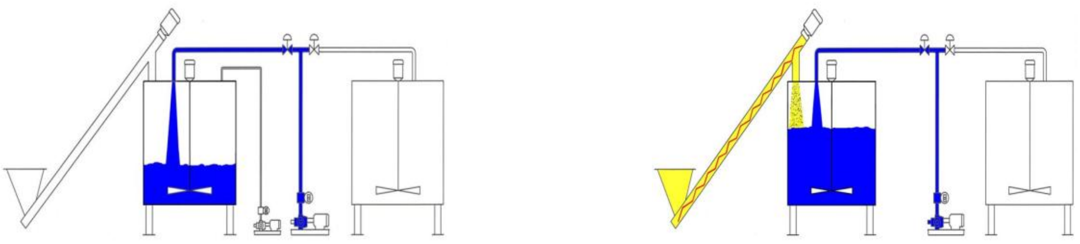
3. PRODUCTION MANAGEMENT

3.1. Modification with SBS

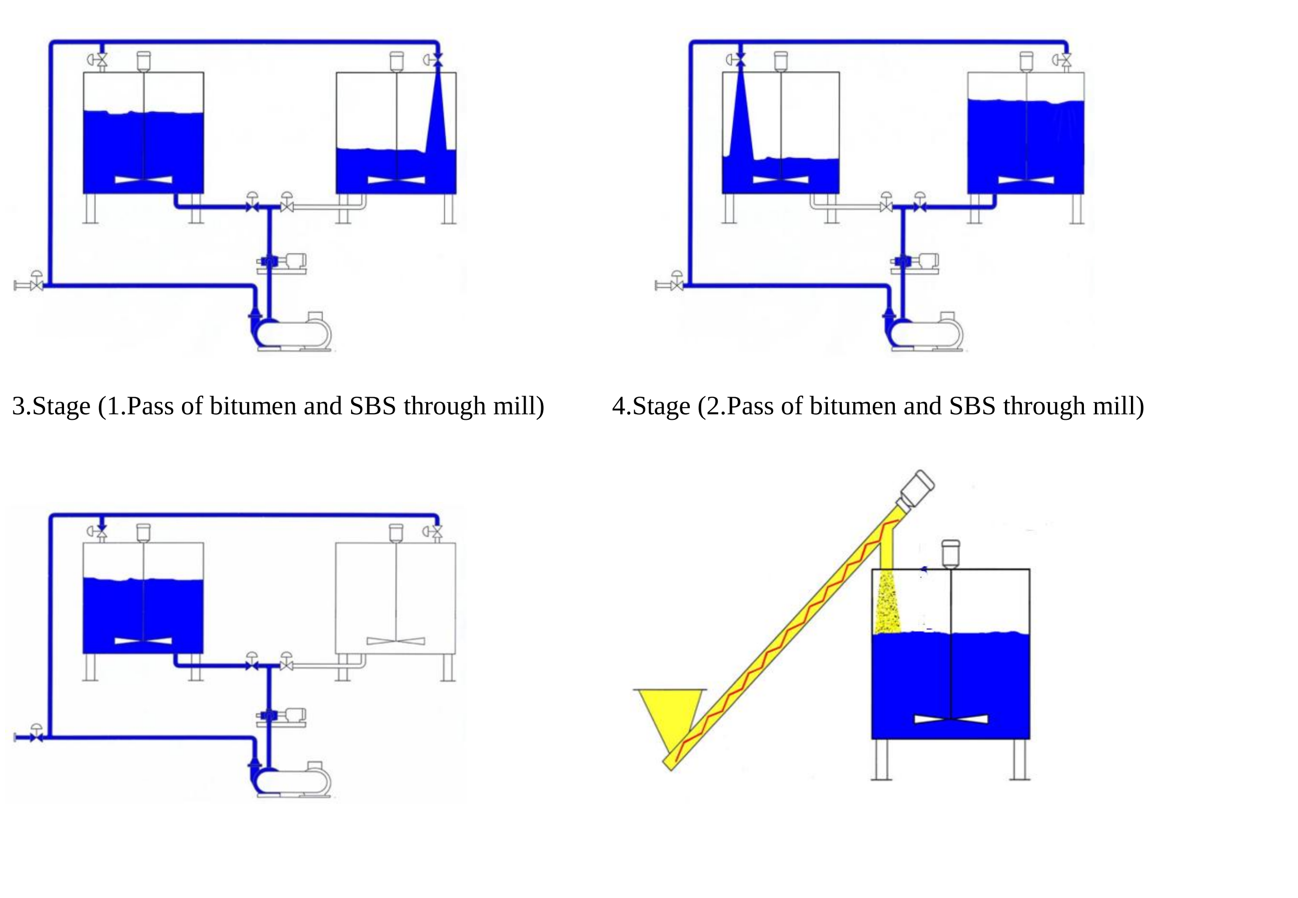
In the first production at 180-190 °C , 50/70 penetration bitumen, calcite and SBS were used and measurements were taken during the production process.

In the second production, conducted in same temperatures, 50/70 penetration bitumen, calcite, SBS polymer and granulated rubber were used and measurements were taken during the production.

The modification stages with the SBS and calcite addition is shown in figure 1 and the specifications of the bitumen produced at this stage are given in Table 5.



1.Stage (Transfer of bitumen to the tank) 2.Stage (SBS supplement to the tank)



3.Stage (1.Pass of bitumen and SBS through mill) 4.Stage (2.Pass of bitumen and SBS through mill)

5.Stage (3.Pass of bitumen and SBS through mill) 6.Stage (Calcite supplement)

Figure 1. Stages of the modification and calcite supplement

Table 5: Characteristics of bitumen, modified by SBS Co-polymer, with calcite supplement

Properties	**Unit**	**Test Method**	**Test result**
Penetration	0.1mm	TS EN 1426	45
Softening point	ºC	TS EN 1427	104
Flash point	ºC	TS EN 2592	330
Elastic Recovery	%	TS EN 13398	100
DSR (Pass fail temperature)	ºC	TS EN 14770	88
RTFOT	%	TS EN 12607-1	0.1

3.2. Granulated Rubber Supplement

Granulated rubber addition was done after the 6th stage, which is shown in Figure 1, and emission measurements were taken during the production that is conducted in 180-190 ° C temperature.

Table 6: **Specifications of the calcite and granulated rubber added bitumen modified with SBS co-polymer.**

Properties	Unit	Test Method	Test result
Penetration	0.1mm	TS EN 1426	48
Softening point	ºC	TS EN 1427	103
Flash point	ºC	TS EN 2592	330
Elastic Recovery	%	TS EN 13398	100
DSR (Pass fail temperature)	ºC	TS EN 14770	88
RTFOT	%	TS EN 12607-1	0.2

The technical characteristics of all tested binders with bitumen are given in Table 7.

Table7: Product Characteristics Comparison Table

Bitumen specifications	Original bitumen	Original bitumen +SBS	Original bitumen +SBS +Calcite	Original bitumen + SBS + Calcite +Rubber
Penetration 0,1mm	55	41	45	48
Softening point °C	49	78	104	103
Flash point °C	332	310	330	330
Elastic Recovery %	…	97	100	100
DSR (Pass fail temperature)°C	64	80	88	88
RTFOT %	0.6	0.1	0.1	0.2

4. INFORMATION ON THE MEASUREMENT SOURCE IN THE FACILITY

4. 1 Emission Sources

The ventilation shaft of the modified bitumen facility with a capacity of 12 tones/hour in the Habibler Factory is given as the emission source. The emission source and emission parameters are given in Table 8.

Table 8 : Emission Sources

Source No	Emission Source	Emission Parameters
1	Ventilation Shaft Of Modified Bitumen Facility	Dust, VOC

5. MEASUREMENT METHODS, MEASUREMENT EQUIPMENTS AND STANDARDS USED IN THE FACILITY

5.1. Measurement Methods

The methods and related standards, applied in the measurements carried out in the facility, are given in Table 9.
TS EN 13649,which is common and widely accepted method in Turkey, was used to determine changes in mass of organic compounds.

Table 9. Measurement Method and Related Standards

Measurement Area	Parameter	Method Title	Standard Codes
Emission Measurement	Volatile Organic Compounds and Steam Determination	Determination of Changes in Mass of Organic Compounds in Gaseous Form by Active Carbon and Solvent Desorption Method	TS EN 13649
	Particle Substance	Gravimetrical Method	TSE ISO 9096:2004

5.2 Measurement Equipment

TCR TECORA branded D.D.S and ISOST ACK BASIC dust sampling equipment have been used in the measurements carried out in the facility.

5.3 Institution taken the measurements

The measurements of emission and air quality within the vicinity are carried out by the accredited institution KONÇEV Engineering and Measurement Services Ltd. Co. Environment Laboratory (Turkey).

6. RESULTS AND EVALUATION OF THE MEASUREMENTS

During the production process, carried out by using penetration grade bitumen, calcite and SBS polymer (Styrene-butadiene-styrene) , the VOC (volatile organic compounds) and dust measurements (according to the standards given in Table 9.0) in the emission source were taken in accordance with the shaft dimension and measurement height requirements.
Three measurements were obtained in accordance with related regulations of Ministry of Science, Industry and Technology in Turkey and the average values were used for the evaluation of the data. Results are given in Table 10a and 10b.
The class analysis of the VOC species detected in highest concentrations was presented in Table 10b and Table11b. Also other VOCs with very low concentrations were considered negligible.

Table 10a –Emission source: Modified Bitumen Facility Ventilation Shaft - Measurements made after productions with bitumen, calcite and SBS addition

SHAFT No.	**1**				
	Shaft Dimension (cm)	Height above ground level (m)			Height above roof level (m)
	34x31	9			Independent
	1.Measurement	2.Measurement	3.Measurement	Average	Limit Value (Max)
Date of Measurement	27.07.2011				
Gas Temperature (°C)	32.88	32.73	32.63	32.75	
Gas Velocity (m/sn)	7.81	7.72	7.19	7.57	≥4m/sn
Shaft cross section (m^2)	0.46				
Flow rate of gas (m3/hour)	13018	12868	11985	12624	
Flow rate of the dry shaft gas (m3/hour)	10001	9891	9217	9703	
Pressure (Kpa)	89.63	89.63	89.65	89.64	
VOC Concentration (mg/Nm^3)*	7.6974	15.6048	20.0271	14.4431	300
VOC Concentration (kg/hour)	0.0770	0.1543	0.1846	0.1386	30
Dust Concentration (mg/Nm^3)	1.4800	0.6100	2.6500	1.5800	165
Dust concentration (kg/hour)	0.0148	0.0060	0.0244	0.0151	30

* "Nm^3" means normal cubic meter.

Table 10b – Modified Bitumen Facility Ventilation Shaft - Class Analysis of Detected Volatile Organic Compounds

Parameter	**Concentration (mg/Nm^3)**				**Limit Value Maximum (mg/Nm^3)**
	1. Measurement	2. Measurement	3. Measurement	Average	
n-Heptane	0.067846	0.00000	0.016459	0.028102	300
n- Butyl acetate	0.025947	1.957337	0.017634	0.666973	300
Toluen	0.395627	0.130651	0.207763	0.244680	150
Cyclohexanol	0.485317	2.10244	0.744055	1.110604	300

Later on , granulated rubber has been added to the compound consisting of these three substances, and measurements taken from the same source; the results are given in Table 11a and Table 11b.

Table 11a. Emission Source: Modified Bitumen Facility Ventilation Shaft- Measurements made after productions with bitumen, calcite, SBS and granulated rubber addition

SHAFT No.	**1**				
	Shaft Dimension(cm)	Height above ground level (m)			Height above roof level (m)
	34x31	9			Independent
	1. Measurement	2.Measurement	3.Measurement	Average	Limit Value(Max)
Date of Measurement	27.07.2011				
Gas Temperature(°C)	30.59	30.98	31.01	30.86	
Gas Velocity (m/sn)	7.81	7.72	7.19	7.57	≥4m/sn
Shaft cross section (m^2)	0.46				
Flow rate of gas (m3/hour)	13018	12868	11985	12624	
Flow rate of the dry shaft gas (m3/hour)	10167	10037	9347	9850	
Pressure (Kpa)	89.99	89.99	89.99	89.99	
VOC Concentration (mg/Nm^3)	16.4730	38.9385	7.3252	20.9122	300
VOC Concentration (kg/hour)	0.1675	0.3908	0.0685	0.2089	30
Dust Concentration (mg/Nm^3)	2.5600	4.6320	3.6340	4.2753	165
Dust concentration (kg/hour)	0.0260	0.0465	0.0527	0.0417	30

Table 11 b – Modified Bitumen Facility Ventilation Shaft- Class Analysis of Detected Volatile Organic Compounds

Parameter	**Concentration (mg/Nm^3)**				**Limit Value Maximum (mg/Nm^3)**
	1. Measurement	2. Measurement	3. Measurement	Average	
n-Heptane	0.051406	0.027556	0.009397	0.029520	300
n- Butyl acetate	0.026112	5.047103	0.020806	1.698007	300
Toluen	0.116423	0.253984	0.034827	0.135078	150
Cyclohexanol	0.655367	4.129215	0.529796	1.771459	300

* The limit values, shown in Table 10.a, Table 10. b and Table 11.a Table 11.b, are based on the values given in Regulation for Protection Against Industrial Air Pollution.

7. RESULTS

In the modified bitumen facility in Habibler Asphalt Facility, the VOC (volatile organic compound) and dust concentrations have been measured in the ventilation shaft during the 1st production with bitumen, calcite and SBS mixture and 2nd production with additional rubber supplement and the results are given in Table 12.

Results revealed that the values of released VOC (volatile organic compounds) and dust concentrations to the environment during the production with SBS , bitumen and calcite is less than the concentration of same substances released after granulated rubber addition to the mix.

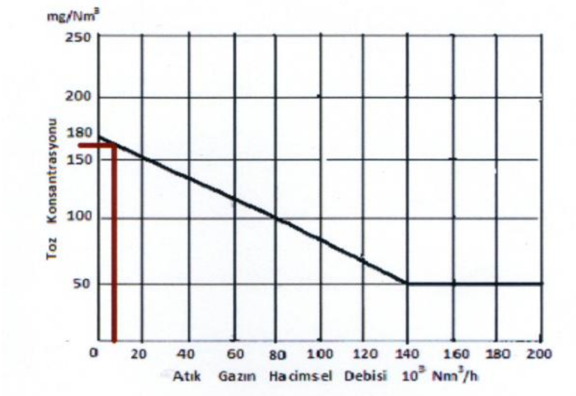


Figure 2: Dust Emission Limits

Obtained values of both products were compared against the limiting values given in the valid Regulation for Protection Against Industrial Air Pollution in our country; and it has been observed that resulting values for both products are far below the limiting values given in the legislation, and therefore well within the limits. (Figure 2 and Table 12)

Table 12. Comparison of Measured Results of Ventilation Shaft in 1st. and 2nd production with limit values given in Regulation for Protection Against Industrial Air Pollution

	1. Production By using Bitumen+Calcite+SBS	**2. Production By using Bitumen+ Calcite +SBS + Granulated Rubber**	**Limit Value Maximum (Mg/Nm^3)**
VOC Concentration (mg/Nm^3)	14.44	20.91	300
DUST Concentration (mg/Nm^3)	1.58	4.275	165

Different regulations or limitations can be valid in different countries, thus it would be appropriate to evaluate the results according to the local regulations of the subjected country.

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