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EFFECT OF THE WEATHER IN THE AGING OF ASPHALSTS BY XRD

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ABSTRACT

Asphalt is a sticky, black and highly viscous liquid or semi-solid that is presented in most crude petroleum and in some natural deposits. As is well known, asphalt has been the preferential choice in pavement construction since excellent utility of pavement, however, as other organic substances, it is also subjected to aging phenomena evolving with time. Asphalt aging is one of the principal factors causing deterioration of asphalt pavements. The photodegradation of asphalts must be considered in the study of the performance of asphalt pavement, especially in geographical regions where high solar radiation intensity occurs. It has an important influence in asphalt aging in tropical places as Brazil. Many methods have been applied to simulate aging of bitumen. It was just a simulation but not real aging asphalt. In this study we submitted the asphalt to the weather as sun and rain. Periodically, during 430 days, the XRD profiles were done and the results analyzed. The scattering measurements were carried out in θ-2θ reflection geometry using a powder diffractometer Shimadzu XRD-6000. Scans were typically done from 8^o to 28^o every 0.05^o. The parameters FWHM and peak centroid were analyzed. From 0 until 180 days the aging was faster. The peaks were marked and analyzed with the pass of time. The crystallinity of asphalt increase with weather exposition. Some angles of profiles changed the position indicating change of atomics plans.

1. INTRODUCTION

Asphalt aging is one of the principal factors causing deterioration of asphalt pavements. It is prone to go fragile and stiff due to exposure to heat, oxygen, and ultraviolet (UV) light during storage, mixing, transport and laying down, as well as in service life [1-2]. These aging processes lead to decrease of asphalt properties such as high-temperature rutting and low temperature cracking, and shorten the lifetime of pavement [3]. The photodegradation of asphalts must be considered in the study of the performance of asphalt pavement, especially in geographical regions where high solar radiation intensity occurs [4]. Many methods have been applied to investigate the process of asphalts aging and several studies applied standard rolling thin film oven (RTFO) test and pressure aging vessel (PAV) test to simulate the short-term and long-term aging of bitumen [1-8]. The aging asphalt was simulated; this was just a simulation but not real aging asphalt. In this study we submitted the asphalt to the weather as sun and rain. Periodically the XRD profiles were done and the results analyzed. After this, the same asphalt sample return to exposition, until that new profile, in the new time, will be obtained. The XRD showed be possible differentiate asphalts of different standards classifications through peak centroid and others parameters [9]. The main objective of this work is to observe the effects caused from the weather in the Brazilians petroleum asphalts cements by the XRD.

2. MATERIALS AND METHODS

2.1. Cement Asphalt of Petroleum

In refineries producing asphalt, crude oil is distilled initially on atmospheric pressure in order to separate the more volatile fractions of heavier. Then, the heavier fractions are subject to the vacuum distillation. The residue of this distillation is called asphaltic waste, and if it is framed in the Brazilian specifications is replaced by the name of Asphaltic Cement of Petroleum or CAP. It's follow the standard Brazilian DNIT 031/2006- ES. The CAP is in ambient temperature semi-solid and black. The Brazilian petroleum has good viscosity for production of asphalt. The samples of Brazilian asphalt cement CAP 50/70 were obtained from two PETROBRAS Refineries, President Getúlio Vargas Refinery (REPAR) and Paulinia Refinery (REPLAN).

2.2. X-Ray Diffraction

The scattering measurements were carried out in θ-2θ reflection geometry using a powder diffractometer Shimadzu XRD-6000 at the Nuclear Instrumentation Laboratory (COPPE/UFRJ), Brazil. The tube has a cobalt target (E = 8.047 keV) and works at 40 kV and 30 mA. The sample is placed in the aluminum sample holder within a circular depression with 2.5 cm of diameter and volume equal to 0.5 cm^3. A 1^o scatter slit (SS) and a 0.30 mm receiving slit (RS) collimate the incident and the diffracted beam, respectively. Then the beam reaches a curved graphite monochromator and enters a NaI(Tl) scintillation detector. Scans were typically done from 8^o to 28^o every 0.05^o. The measured characterization parameters, peak centroid and FWHM were associated with the kind of asphalt. The peak center had the standard deviation higher than peak centroid, therefore the peak centroid was chosen in this research.

3. RESULTS

Figures 1 and 2 shown the mean profiles obtained from CAP 50/70 produced by REPAR and REPLAN Refineries. The profiles were obtained in 0, 60, 120, 180, 210, 330, 390 e 430 days. Each profile, in each date, is an average profile from ten profiles (n=10).

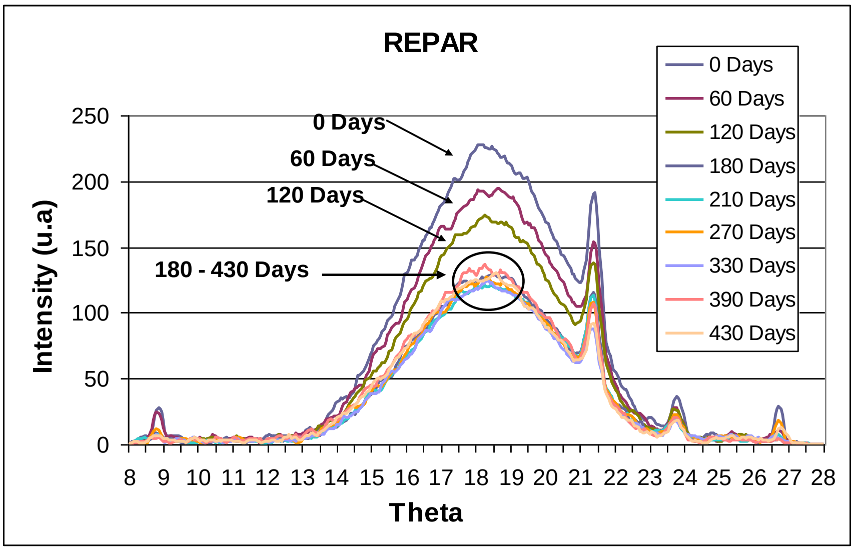

Figure 1. Means profiles from CAP 50/70 by REPAR Refinery in each time.

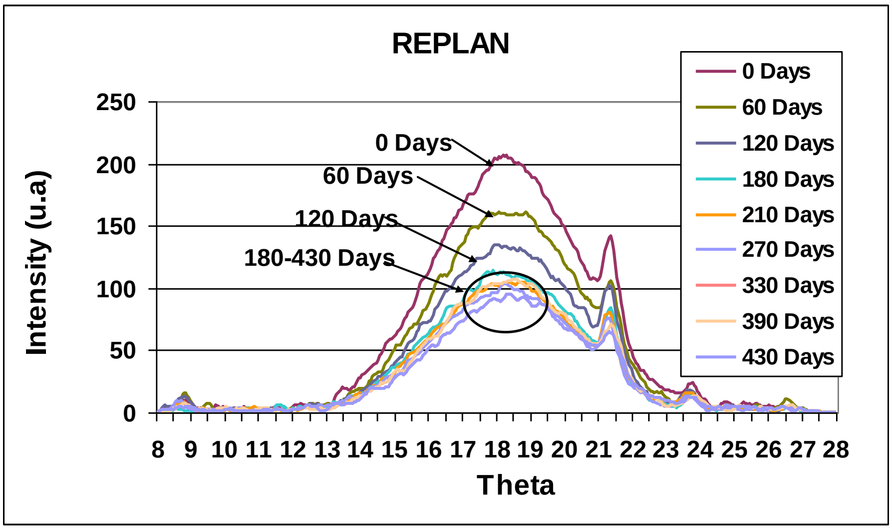

Figure 2. Means profiles from CAP 50/70 by REPLAN Refinery in each time.

The figure 1 and 2 shows a higher intensity reduction, between 0 and 180 days, of broad peak around 18 degrees. From 180 until 430 days the peak intensity of broad peak tends to stabilize. This reduction indicates the possible reduction of volatile fraction that compound the asphalt. It's more intensity in begin of exposition. The table 1 shows the peak centroid and FWHM parameters obtained from XRD profiles in each time.

Table 1. Parameters obtained from XRD profiles in each time of weather exposition.

Time (exposition)	**REPAR**				**REPLAN**			
	Peak Centroid		**FWHM**		**Peak Centroid**		**FWHM**	
Days	Value	SD	Value	SD	Value	SD	Value	SD
0	18.48	0.15	5.63	0.36	18.49	0.19	5.23	0.35
60	18.44	0.16	5.46	0.49	18.54	0.39	5.05	0.43
120	18.48	0.20	5.48	0.39	18.69	0.43	5.06	0.92
180	18.49	0.19	5.53	0.35	18.55	0.39	5.41	0.45
210	18.49	0.18	5.60	0.26	18.59	0.53	5.17	0.55
270	18.50	0.20	5.53	0.35	18.62	0.47	5.44	0.38
330	18.46	0.22	5.39	0.42	18.60	0.25	5.36	0.43
390	18.35	0.23	5.25	0.39	18.40	0.34	5.27	0.44
430	18.32	0.17	5.57	0.38	18.52	0.38	5.21	0.57

The mean values of parameters were compared using the analysis of variance (ANOVA) test, Bonferroni's test. There is no significant difference between REPAR CAP50/70 and REPLAN CAP50/70. It's a good results because it's have the same standards classification. The average peak centroids are $18.45^{o} \pm 0.19^{o}$ for REPAR and $18.56^{o} \pm 0.37^{o}$ for REPLAN. These are good results because from 0 days until 430 there is no significant difference in the value of peak centroid. It's show the peak centroid is a excellent classification parameters to fresh or aging asphalts because not change significantly with the time.

The tables 2 and 3 shows the peaks marked in profiles with the objective of observe their behaviors during the aging process.

Table 2 – Peaks obtained from fresh and aging REPAR CAP 50/70.

Fresh REPAR (T = 0)			Aging REPAR (T = 430 Days)		
Peak Centers X	Peak Centers Y	I/Imáx	Peak Centers X	Peak Centers Y	I/Imáx
8.50	6.48	0.03	8.20	1.97	0.02
8.85	28.00	0.12	8.75	6.73	0.05
9.25	6.78	0.03	9.25	3.60	0.03
9.90	4.15	0.02	9.90	5.10	0.04
10.05	3.81	0.02	10.40	2.83	0.02
10.40	2.96	0.01	10.80	3.33	0.03
10.80	5.04	0.02	11.20	1.93	0.01
11.15	2.26	0.01	11.50	3.73	0.03
11.50	3.59	0.02	12.15	3.57	0.03
12.05	7.04	0.03	12.60	7.17	0.06
12.35	6.48	0.03	12.80	5.80	0.04
12.50	6.93	0.03	13.25	8.53	0.07
12.70	6.78	0.03	15.20	50.17	0.39
13.20	12.63	0.06	17.95	124.57	0.96
14.10	34.96	0.15	**18.55**	**130.13**	**1.00**
14.25	36.19	0.16	19.00	121.20	0.93
17.40	202.04	0.89	20.45	78.97	0.61
18.05	**227.56**	**1.00**	21.35	92.03	0.71
18.45	226.07	0.99	22.90	9.40	0.07
18.80	218.81	0.96	23.05	9.10	0.07
19.25	206.67	0.91	23.80	18.57	0.14
19.45	203.22	0.89	24.30	3.17	0.02
21.40	191.37	0.84	24.90	5.00	0.04
22.95	20.15	0.09	25.40	6.07	0.05
23.75	36.37	0.16	25.70	5.43	0.04
24.40	3.15	0.01	25.85	5.70	0.04
24.75	8.30	0.04	26.15	4.40	0.03
25.10	4.96	0.02	26.75	12.33	0.09
25.45	7.04	0.03	27.30	1.03	0.01
25.60	7.22	0.03			
25.75	6.15	0.03			
26.70	28.89	0.13			
27.20	1.30	0.01			
27.40	0.96	0.00			

All possible peaks from figure 1 were marked by the ORIGIN program and were show in table 2. From 33 peaks marked in the fresh asphalt profile, only 6 were repeated in the same angle position in the aged asphalt profile (9.25^{o}, 9.90^{o}, 10.40^{o}, 10.80^{o} and 11.50^{o}). 21 peaks marked in the fresh asphalt and 23 peaks in the aged asphalt were less than 10% of highest peak intensity found in each profile. Angle 8.85^{o}, 21.40^{o}, 23.75^{o} and 26.70^{o} change the position to 8.75^{o}, 21.35^{o}, 23.80^{o} and 26.75^{o} what indicates possible change the distance between atoms plans given by law of Bragg.

Table 3 – Peaks obtained from fresh and aging REPLAN CAP 50/70.

Fresh REPLAN (T = 0 Days)			Aging REPLAN (T = 430 Days)		
Peak Centers X	Peak Centers Y	I/Imáx	Peak Centers X	Peak Centers Y	I/Imáx
8.85	10.07	0.05	8.20	2.10	0.022
9.30	4.17	0.02	8.65	4.70	0.050
9.75	5.83	0.03	8.95	4.70	0.050
9.95	4.27	0.02	9.35	2.13	0.022
10.55	4.33	0.02	9.70	2.20	0.023
10.70	3.43	0.02	10.15	3.60	0.038
11.05	3.47	0.02	10.45	1.60	0.017
11.50	5.40	0.03	10.65	1.67	0.018
12.25	7.33	0.04	11.25	2.60	0.027
12.55	7.67	0.04	11.55	2.73	0.029
13.45	19.97	0.10	12.00	2.93	0.031
17.20	175.80	0.85	12.50	5.80	0.061
18.30	**206.33**	**1.00**	13.25	7.03	0.074
18.65	200.67	0.97	13.60	7.23	0.076
20.85	108.47	0.53	14.35	20.63	0.218
21.35	141.53	0.69	15.15	30.83	0.326
23.35	15.97	0.08	15.65	42.03	0.444
23.75	23.60	0.11	17.30	81.33	0.859
24.80	8.27	0.04	17.95	91.40	0.965
25.25	7.90	0.04	**18.35**	**94.70**	**1.000**
25.60	7.20	0.03	18.75	92.73	0.979
26.00	5.43	0.03	19.25	87.33	0.922
26.40	4.57	0.02	21.30	64.63	0.682
26.90	3.43	0.02	23.65	12.63	0.133
27.25	0.73	0.05	24.55	4.57	0.048
27.50	0.50	0.02	24.75	5.53	0.058
			25.25	5.17	0.055
			26.05	3.70	0.039
			26.35	5.00	0.053
			26.95	3.17	0.033

All possible peaks from figure 2 were marked by the ORIGIN program and were show in table 3. There were not repeated peak from fresh asphalt in aged asphalt profile. The program marked 26 peaks in the fresh asphalt and 30 peaks in the aged asphalt but only 7 peaks from fresh asphalt and 15 peaks from aged asphalt had more that 10% of value of highest peak intensity found in each case.

The visible peaks in the figure 2 can be identified in the table 3. Angles 8.85^o, 21.35^o and 23.75^o may change the position to 8.95^o. 21.30^o and 23.75^o what indicates possible changed of distance between atoms plans given by law of Bragg.

The figure 3 show the variation of crystallinity in the time. It was occurred, but not linear increase as expected. The crystallinity of REPAR passed of 10.87% (0 days) to 12.22% (430 days) and the crystallinity of REPLAN passed of 10.41% (0 days) to 12.60% (430 days). This represents an increase of 12.42% and 21.04% to REPAR and REPLAN respectively.

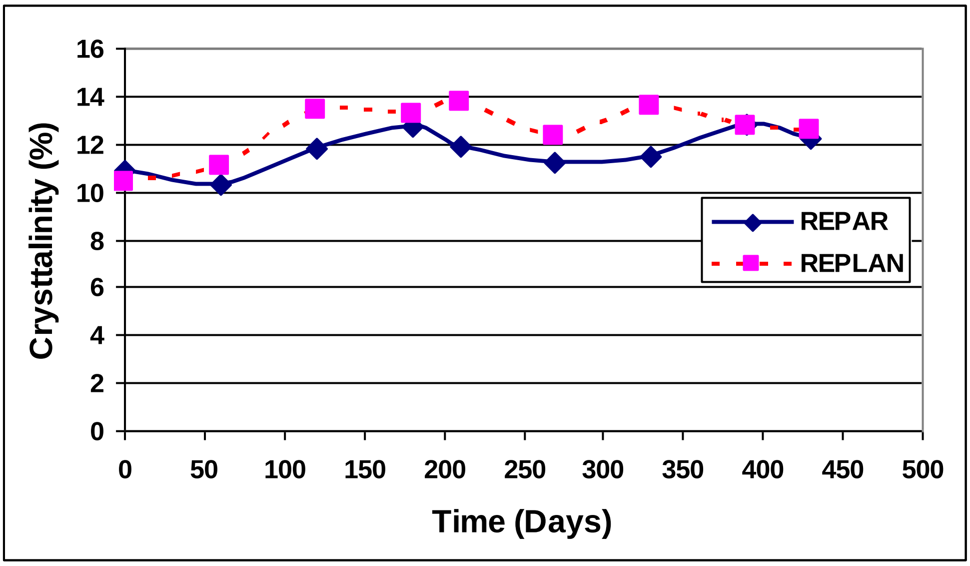

Figure 3. The variation of crysttalinity with the time.

4. CONCLUSIONS

X-ray diffraction is a good tool to identification of petroleum asphalt cement because the peak centroid value, best parameter to asphalt identification, not changed significantly with the pass of the time, with weather exposition for 50/70 asphalt produced by REPAR and REPLAN Refineries. It's show XRD efficient for asphalt identification, fresh or aged. The asphalt crystallinity grow up with the time of weather exposition but not of linear form as expected. The increase of crystallinity can be relationship with increase of viscosity characteristics of aging petroleum. Some angles changed the position what indicates possible changed of distance between atoms plans given by law of Bragg. Future analyses will search the relation among variation of values intensities with the variation of the chemical components in the material because the aging is generally associated with oxidation at the molecular level. Analysis of the results obtained in this work indicates that the X-ray diffraction is a good tool in the study of aging of petroleum asphalt cement.

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