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DEVELOPMENT OF THE ENGINE OIL SEAL COMPATIBILITY TEST

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Abstract

Engine oil seal compatibility tests according to VW PV 3344 standard were carried out. The visual evaluation of test-method was developed. Seven photographs were taken of cracked fluoroelastomer test-pieces and digital image processing was applied. The so called Area Covering Ratio (ACR) was calculated and its statistical properties were investigated. Based upon the results four statistically different new categories of cracked test-pieces could be established by using the ACR. This new evaluation method was found to be simple, quick, reliable and cheap, which resulted in better ability for differentiation among similar engine oils and additives in seal compatibility tests. It was demonstrated by Environmental Scanning Electron Microscope (ESEM) that pre-ageing caused little cracks on the surfaces of fluoroelastomer. The basic dispersants catalyzed fluorine elimination was proved by the decreasing fluorine contents, which showed good correlation to the rate of the attack, i.e. to the ACR value of test-pieces.

Keywords: seal compatibility; VW PV 3344; Area Covering Ratio (ACR) ; fluorine content.

1. Introduction

Different flexible elastomer seals and gaskets are commonly used in all internal combustion engines of automotives, in particular to prevent contamination and lubricant leakage at those points where moving parts, such as the crankshaft, are in contact with the engine[1]. The main types of these polymer materials are fluoroelastomer, polyacrylates, polysiloxanes and nitrile rubber. The prevention of the deterioration of said seals, gaskets and clutch face plates made from (fluoro)elastomer is very important from the viewpoint of both reliable operation and environmental aspects. There are two primary mechanisms by which seal damage can occur, abrasion due to solid contaminants and the attack of various engine oil compounds. Abrasive damage is not common since most engines have effective lubricant filtration system. The lubricant-related damage can occur when some of various lubricant components diffuse into the seals. This will either cause a change in the hardness, thereby leading to swelling and/or elongation, or extract the plasticizer agent used to impart flexibility and strength to polymeric materials[1-3].

The unconventional base oils (highly refined hydrocracked and synthetic oils) can seriously deteriorate the elastomer seals by extracting their plasticizer compounds causing embrittlement, shrinkage and leakage or penetrating into the elastomer causing swelling. To solve this problem optimal balance of base oils should be applied or so called seal swelling agents (such as dioktyl-sebacate, dihexyl-ftalate, tridecyl-alcohol and organic phosphates, polybutenyl succinic anhydride etc.) have to be used[1, 4].

The elastomer seals and gaskets, especially fluoroelastomer can be highly attacked under engine operating conditions by nitrogen containing dispersants, which are used in engine oils in great concentrations (6-10%). These additives contain strongly basic amino groups and in case of fluoroelastomer, which have otherwise high thermal stability and chemical resistance, base-catalyzed elimination of hydrofluoric acid occurs, with the

consequent formation of unsaturations, and thus the deteriorated elastomer loses elasticity and elongation until it no longer possesses sealing capacity. These problems can easily be occurred due to the presence of low molecular weight succinimides, succinamides and free amines, which can be found in dispersants. Because of their high polarity and small size, these molecules are more likely to diffuse into the seal material and alter its properties. Removal of the free amine and low molecular weight succinimides improves seal performance[1, 5-8].

In Diesel engines higher soot loading caused by exhaust gas recirculation (EGR), higher flame temperature, longer drain interval etc. require higher detergent and dispersant concentrations in engine oils to maximize soot handling. That is the reason why seal compatibility is greatly highlighted. In general, for a given polyisobutenyl-succinimide type dispersant, a higher nitrogen content gives better dispersancy and soot handling but poorer elastomer compatibility. On the other hand, as the operating temperature of the engine rises the rate of the decomposition of the seal rises proportionately. In the literature a lot of process is described to enhance the seal compatibility of dispersant additives by post-treatment while keeping the good dispersancy[1, 3, 9].

The balance between soot handling and seal compatibility has provided lubricant formulators with significant challenges over the past ten years, especially as seal testing is a major part of the engine oil approval process in Europe[10]. There are numerous ASTM, DIN, ISO, CEC and local standards for investigation of the seal compatibility of engine oils and these can be found in the requirements of performance levels of engine oils (mainly for Diesel engines). Volkswagen has his own standard, VW PV 3344 for fluoroelastomer. In these tests standard test-pieces, made from the most commonly used elastomer, are immersed into the investigated engine oil for a given period of time and at a given temperature. After immersion the changes of the properties (tensile strength, elongation at rupture, volume and hardness) are evaluated. Beyond these, the presence of possible surface cracks is very important, especially in case of fluoroelastomer. The evaluation in VW PV 3344 method is visual and carried out at 100% elongation. The visual method can be adapted for determining that the tested engine oil passes or fails the seal compatibility test but their ability for differentiation is poor (no cracks, surface cracks or cracks).

For improving the additive development it is essential to improve the ability for differentiation and the accuracy of the visual evaluation method in order to differentiate engine oils with very similar seal attacking properties from each other. Our aim was the development of the visual evaluation method of VW PV 3344 seal compatibility test.

2. METHODS AND MATERIALS

Seal compatibility tests were carried out according to VW PV 3344 standard. S3A test-pieces made of AK-6 fluoroelastomer were used. After pre-ageing at 150°C for 24 hours S3A specimens were immersed into engine oil (ratio of volume of test-pieces and engine oil was 1:80) at 150°C for 168 hours. Stainless steel racks for hanging the test-pieces were made according to VW PV 3323. After 8 day pre-ageing and immersion, tensile tests were carried out according to DIN 53504 by INSTRON 3344 apparatus. One of the test-pieces was always evaluated at 100% elongation in order to find cracks on the surface. Photographs were taken by OLYMPUS C700 Ultra Zoom digital camera. Shore A hardness was determined by INSTRON Shore S1 digital apparatus. The surface and elemental composition of the test-pieces were evaluated by Philips XL30 Environmental Scanning Electron Microscope (ESEM). Almost 50 experimental engine oils were blended from commercial additives and base oils for seal compatibility tests.

3. RESULTS AND DISCUSSION

First of all the precision of the tensile test and seal compatibility test were studied. The original and pre-aged S3A specimens were tested (7 independent tensile tests per batch, 3 different batches) and according to data in Table 1 the repeatability and reproducibility requirements of DIN 53504 tensile test standard were fulfilled. The original test-pieces from different batches resulted in higher reproducibility in tensile tests but it was concluded that differences in the quality of fluoroelastomer and the test

methods between the two laboratories caused this phenomena. Based on the results of the reference engine oil (SD), which were used as internal standard, and four experimental engine oils (DM 1-4), which were tested in two independent laboratories (Figure 1), the precision of the whole seal compatibility test (including tensile test) was found to be good enough.

After precision studies the seal compatibility of nearly 50 engine oils were tested and in lot of cases cracks could be observed visually on the surfaces of specimens. It was found that cracks firstly appeared on the side of test-pieces, especially on the edges where the elastomer was easily attackable due to shaping. At 100% elongation, seven photographs were taken of cracked specimens. We attempted to take similar photographs, same adjustment, brightness and position. In all cases the important 40 mm sections with cracks were photographed from both sides. Thus in the pictures lower edge of the near side and upper edge of the further side appeared with the cracks (Figure 2). After taking photographs from both sides all of the four cracked edges appeared. This meant that in the further evaluation all cracked edges were taken into account, thereby more representative sampling could be achieved. Then the photographs were processed by Adobe Photoshop CS2 software and after this digital image processing the image of test-pieces became rectangle shaped but the lower and upper side were wavy and irregular due to cracks (Figure 2). By the help of Adobe Photoshop CS2 software the area of the images in pixels could be obtained.

It was assumed that the more cracks were on a test-piece the less area of the regular rectangular was covered by the irregular image of test-piece. Therefore the following so called Area Covering Ratio (ACR) was calculated for cracked test-pieces:

$$ACR,\% = 100 \cdot \frac{area\ of\ cracked\ elastomer\ in\ pixel}{area\ of\ rectangular\ in\ pixel} \quad (1)$$

Table 1 Precision of tensile test and seal compatibility test

Properties	Original S3A			Pre-aged S3A		After immersion into engine oil SD*		After immersion into engine oil DM 1-4**		Requirements DIN 53504		Requirements PV 3344
	Value	Rep.	Repr.	Value	Rep.	Value	Rep.	Value	Repr.	Rep.	Repr.	Value
Load at break, N	124.1	4.8	13.0	123.8	5.0	83.7	7.6	86.5-103.0	9.1	-	-	-
Tensile strength, MPa	15.5	0.6	1.6	15.5	0.6	10.4	0.9	10.8-12.9	1.1	1.3	1.9	min. 7
Change in tens. strength, %	-	-	-	-0.2	3.8	-33	5.9	-17-(-31)	10.6	-	-	max. 60
Elongation at break, mm	103	2.1	11.0	98	2.2	68	2.2	57-76	4.1	-	-	-
Elongation at break, %	395	9.9	26.1	372	12.2	228	10.4	173-264	20.5	27.5	53.1	min. 160
Change in elongation, %	-	-	-	5.8	3.3	-42	2.6	-33-(-56)	2.6	-	-	max. 50
Shore A hardness, points	70.2	1.1	-	70.3	0.3	71.5	0.4	71.5-71.9	-	-	-	-
Cracks, visual	no	-	-	no	no	no	-	no	-	-	-	no

** Reference engine oil (internal standard), four independent measurements*

*** Based on the results of four engine oils obtained in two independent laboratories*

From Equation 1 it could be concluded that in case of more and bigger cracks the ACR is less and in case of specimen without cracks the value of ACR is 100%. The averages and standard deviations of ACR after seven digital image processings per engine oil sample are summarized in Table 2. The previously defined ACR varied between 92.22-99.72% and generally its standard deviation was bigger in case of seriously cracked elastomer (0.41-0.85%). In case of samples with little cracks the standard deviation was smaller, ranged between 0.08-0.30%. Data of Table 2 well present that the random error of the new method was advantageously low, it varied between 0.1-0.7%. To study the systematic error of this new evaluation Student t-probe was carried out. In each case the calculated values were lower than the critical t(95) and also t(99), thus there was no systematic error at 99% confidence level. Nalimov-probe was applied to find outliers from 91 values (13 sample multiplied by 7 parallel ACR), and at 99% confidence level no outliers could be found.

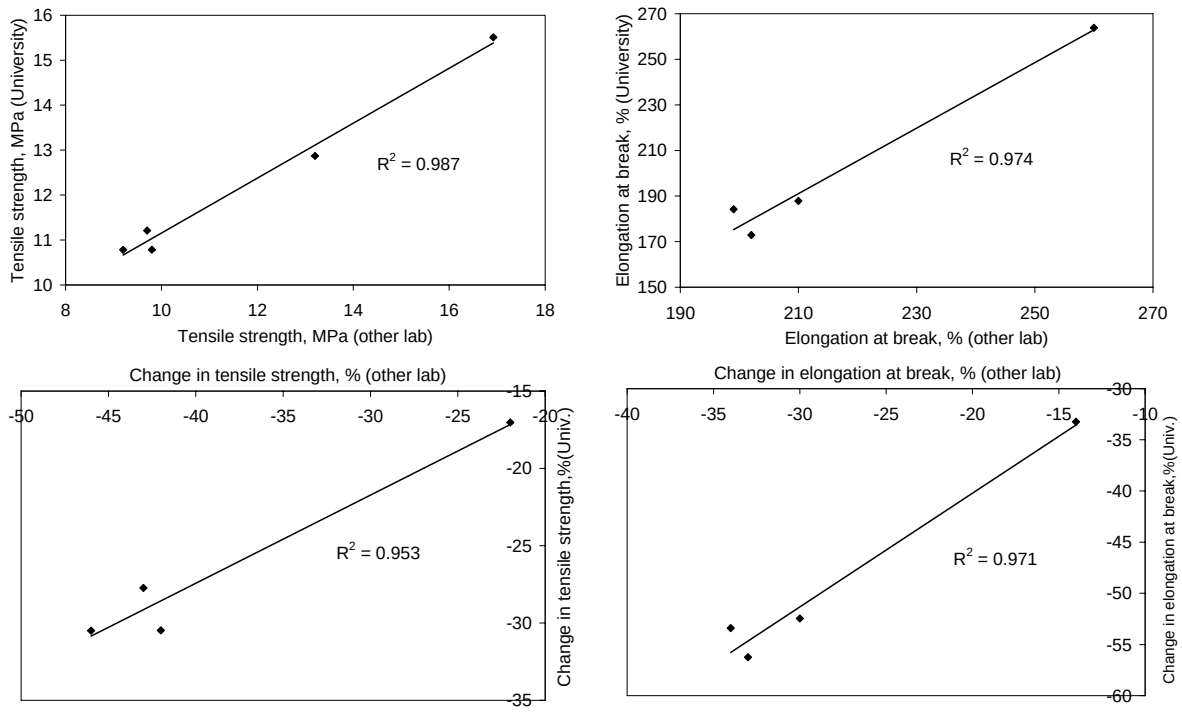

Figure 1 Correlation of the results of the tensile tests (reproducibility)

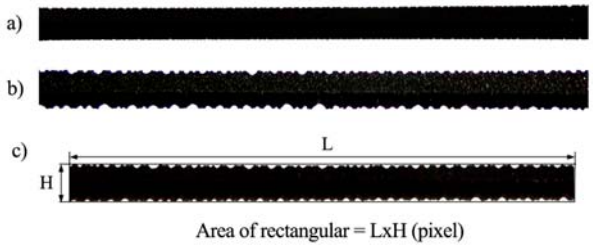

Figure 2 Light cracks (a), serious cracks (b) and the rectangular around the irregular image (c)

Afterwards, in order to achieve bigger ability for differentiation, we tried a second method, namely independent evaluation of the two sides (lower and upper) of seriously cracked test-pieces. The digital image processing was carried out in same way but the lower (upper) side of drawn rectangular was fitted to the lower (upper) side of cracks as Figure 3 shows. The ACR was invariably calculated according to Equation 1. It was assumed that the value of ACR decreases under the previously obtained 92.2-99.8% and the cracked elastomers can be better distinguished. Although the ACR value decreased to 72.77% and 65.80% as we expected but the standard deviation increased to about 5%, while the average difference between the ACR of two sides was nearly 7% (Table 3). It was clearly seen that there was no use evaluating independently the lower and upper sides, because ACR values differed more from each other than in case of firstly described method where both sides and all four edges of cracked test-pieces were taken into account in the evaluation. It was also found that the second method had larger random error than the firstly described method (0.3% vs. 5.3% on the average). The systematic error of the second method was similar than that of the first method. In case of 14 data of second method outlier was found at 95% confidence level but it disappeared at 99% confidence level. Hence the previously described first method, in which both the upper and lower sides were taken into consideration resulted in better precision was chosen for further investigations.

Based on the data of Table 2, namely the average ACR and its standard deviations, four statistically different categories representing the properties of cracked test-pieces aged in engine oils could be established: little (ACR=98.63-99.93%), medium (ACR=96.72-98.63%), many (ACR=93.35-96.72%) and serious (ACR<93.35%) see in Figure 4. Of course, the names of categories refer to the quantity of cracks. In Figure 4 it can also be seen that using this new evaluation method and categories better ability for

differentiation could be achieved in contrast with the visual method where only two categories could be established in case of cracked test-pieces.

Table 2 Average ACR values and statistical data of 7 digital image processings (critical values for 7 samples: t(95)=2.447 and t(99)=3.707)

Sample	ACR, %	Standard deviation	Random error, %	Systematic error (Student t-probe)
M1	92.22	0.85	0.7	2.116
M2	94.41	0.78	0.7	2.140
M3	95.72	0.52	0.5	2.316
M4	95.10	0.41	0.3	1.989
M5	97.64	0.44	0.4	2.370
M6	97.83	0.42	0.4	2.173
M7	99.43	0.24	0.2	2.214
M8	99.72	0.21	0.2	2.174
M9	99.32	0.30	0.3	2.232
M10	99.69	0.08	0.1	2.165
M11	99.65	0.20	0.2	2.182
M12	99.67	0.16	0.1	2.158
M13	99.71	0.18	0.1	2.036

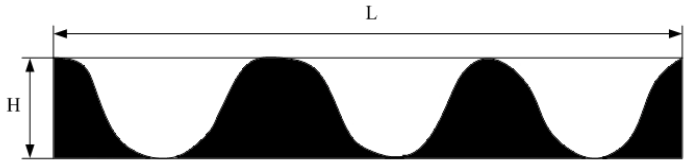

Figure 3 Evaluation according to second method(the rectangular around only one side of the image)

Table 3 Data of evaluation of test-piece of M1 sample according to second method (independent evaluation of upper and lower sides (critical values for 7 samples: t(95)=2.447 and t(99)=3.707, N(95)=1.711 and N(99)=1.983)

Properties	1	2	3	4	5	6	7	Average	S. dev.
ACR									
Lower side	65.99	71.35	71.92	79.42	78.52	74.11	68.12	72.77	4.99
Upper side	59.11	67.23	63.37	63.74	75.63	66.46	65.06	65.80	5.08
Random error, %									
Lower side	9.3	2.0	1.2	9.1	7.9	1.8	6.4	5.4	-
Upper side	10.2	2.2	3.7	3.1	14.9	1.0	1.1	5.2	-
Systematic error (t-probe)									
Lower side	3.597	0.756	0.455	3.521	3.047	0.708	2.470	2.079	-
Upper side	3.487	0.746	1.266	1.071	5.125	0.342	0.388	1.775	-
Nalimov-probe (outlier)									
Lower side	1.359	0.286	0.172	1.331	1.152	0.268	0.933	-	-
Upper side	1.318	0.282	0.479	0.405	*1.937*	0.129	0.147	-	-

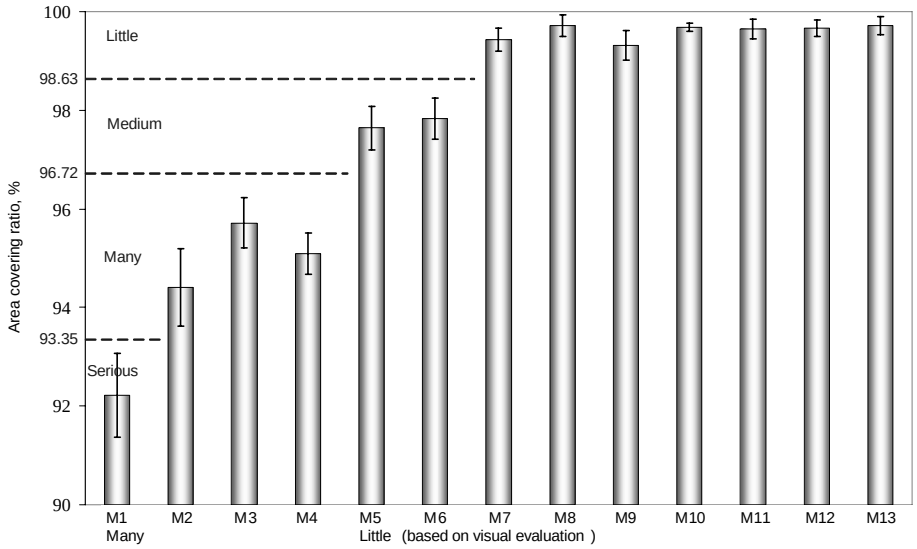

Figure 4 The four new categories based on ACR

For checking the adequate ability for differentiation of the new method a lot of statistical calculations were applied (Shapirov-Wilkinson, Kolmogorov-Smirnov, Anderson-Darling, Wilcoxon tests, F- and t-probes). We wanted to prove that differences were significant among the average ACR values of different categories. Therefore each ACR value of each category had to be compared to each ACR value of neighbouring one or two categories. Firstly, we used the above mentioned methods to prove the normal distribution of ACR values. Without the representation of data of statistical calculations, normal distribution was found in all cases. Based on the data of F-probe (F(AB) in Table 4) the standard deviations of sample pairs were found to be statistically equal at 95-99.97% probability level. After applying the t-probe at the adequate probability level (adequate to the F-probe probability level) it was found that each ACR value of each neighbouring category could be distinguished at 99.97% (in one case only 99%) probability level. The Wilcoxon non-parametric method showed that the probability of difference of ACR values was 98.4%. Therefore it was concluded that by the use of the new evaluation method and the four new categories based on ACR values the cracked test-pieces could be statistically distinguished at high (99% or 99.97%) probability level. The calculated experimental standard deviations of ACR values (Tables 2 and 5) corresponded to 98.7% confidence interval. This was a quite high confidence interval and it was accepted. Complementing the seal compatibility tests with this newly developed, simple, quick and cheap method based on photography and digital image processing, the evaluation of cracks will be more reliable and the development of engine oils and their additives become easier.

By the help of Adobe Photoshop CS2 the histogram of colour could be obtained (Tables 5 and 6). It was concluded if many cracks occurred the most frequent colour moved to brighter colours (higher values) and its standard deviations became higher (5-17), too. Test-pieces with little cracks showed darker colour (lower values) and standard deviations decreased (1-4). Its reason was that the surface of strongly cracked specimens was more heterogeneous which resulted in higher variety of colours.

For investigating the cracks on the test-pieces, the original, pre-aged and some cracked elastomers (after immersion into engine oil) were studied by ESEM. As the results of tensile tests showed (Table 1) the pre-ageing did not alter significantly the mechanical properties of specimens but however in the ESEM pictures (Figure 5b) very small (20-30 μm) cracks could be observed. In case of seriously cracked surface huge cracks with 300-800 μm length were noticed (Figures 5d, 6).

Table 4 Statistical comparison of the ACR values of new categories(critical values for 7 samples: F(95)=4.28, F(99)=8.47, F(99.97)=30.67, t(95)=2.447, t(99)=3.707, t(99.97)=7.456)

Categories	Sample pair	F(AB)	S(AB)	t(AB)	Wilcoxon, p
Serio	M1/M2	1.184	0.820	5.005	0.016
	M1/M3	2.734	0.705us/many	9.270	0.016
	M1/M4	4.237	0.671	8.013	0.016
Many/medium	M2/M5	3.157	0.636	9.497	0.016
	M2/M6	0.286	0.629	10.158	0.016
	M3/M5	1.368	0.480	7.510	0.016
	M3/M6	1.515	0.470	8.401	0.016
	M4/M5	1.133	0.428	11.136	0.016
	M4/M6	1.023	0.417	12.261	0.016
Medium/little	M5/M7	3.497	0.354	9.457	0.016
	M5/M8	4.243	0.347	11.195	0.016
	M5/M9	2.132	0.378	8.297	0.016
	M5/M10	30.436	0.317	12.036	0.016
	M5/M11	4.870	0.343	10.976	0.016
	M5/M12	7.249	0.333	11.361	0.016
	M5/M13	6.012	0.337	11.492	0.016
	M6/M7	3.157	0.340	8.825	0.016
	M6/M8	3.830	0.333	10.631	0.016
	M6/M9	1.925	0.365	7.645	0.016
	M6/M10	27.473	0.302	11.507	0.016
	M6/M11	4.396	0.329	10.401	0.016
	M6/M12	6.544	0.318	10.800	0.016
	M6/M13	5.427	0.323	10.937	0.016

Table 5 Data of 7 digital image processings per sample (most frequent colour, its median and its standard deviation; ACR)

Sample	Cracks*	Statistical properties	Colour value**	Median of colour	S. dev. of colour	ACR, %	Cracks***
M1	Many	Average	47	43	21.37	92.22	Serious
		Median	49	44	22.99	92.05	
		S. dev.	17	18	4.72	0.85	
M2	Many	Average	32	20	18.25	94.41	Many
		Median	31	19	18.00	94.30	
		S. dev.	9	3	2.43	0.78	
M3	Many	Average	28	24	20.92	95.72	Many
		Median	27	24	20.76	95.86	
		S. dev.	6	3	1.91	0.52	
M4	Many	Average	27	17	13.84	95.10	Many
		Median	26	16	13.64	95.08	
		S. dev.	5	2	1.23	0.41	
M5	Little	Average	23	23	13.46	97.64	Medium
		Median	23	23	12.34	97.83	
		S. dev.	2	3	2.74	0.44	
M6	Little	Average	20	18	12.69	97.83	Medium
		Median	19	18	12.68	97.83	
		S. dev.	2	2	0.47	0.42	
M7	Little	Average	24	22	16.49	99.43	Little
		Median	24	22	17.30	99.35	
		S. dev.	2	2	2.23	0.24	
M8	Little	Average	25	21	23.07	99.72	Little
		Median	23	20	17.62	99.82	
		S. dev.	4	3	8.58	0.21	
M9	Little	Average	24	21	17.50	99.32	Little
		Median	23	21	15.19	99.36	
		S. dev.	3	2	4.58	0.30	
M10	Little	Average	23	22	18.30	99.69	Little
		Median	22	21	16.38	99.70	
		S. dev.	3	3	4.66	0.08	
M11	Little	Average	23	21	13.51	99.65	Little
		Median	22	20	13.25	99.75	
		S. dev.	2	2	1.26	0.20	
M12	Little	Average	25	23	14.53	99.67	Little
		Median	25	23	14.29	99.73	
		S. dev.	1	1	0.95	0.16	
M13	Little	Average	23	22	13.89	99.71	Little
		Median	24	22	14.10	99.71	
		S. dev.	2	2	1.09	0.18	
-	No	-	-	-	-	100.0	No

** based on visual evaluation, ** most frequent colour from the histogram of colour (0: black, 255: white), *** new categories based on ACR*

Table 6 Independent evaluation of lower and upper sides of test-piece of M1 oil (7 pictures per side)

Test-piece	Cracks*	Statistical Properties	Colour value**	Median of colour	S. dev. of colour	ACR, %
Lower side	Many	Average	49	38	35.34	72.77
		Median	53	41	35.83	71.90
		S. dev.	20	21	2.27	4.99
Upper side	Many	Average	38	35	35.30	65.80
		Median	44	36	38.18	65.06
		S. dev.	20	17	10.58	5.08

** based on visual evaluation, ** most frequent colour from the histogram of colour (0: black, 255: white)*

ESEM-EDAX investigations were carried out on the surfaces (on 3-4x10^{-6} m^2 and in 5-10 μm depth) and the elemental content was determined, data are summarized in Table 7. According to the literature[5-9] it was found that in case of seriously attacked elastomer significant decrease in fluorine contents took place. Originally the fluorine content was 44.3% when little cracks occurred, after immersion into engine oil, it decreased to 35%. The fluorine content of the seriously attacked elastomer was only 26.1%. The fluorine contents correlated to the rate of the attack, i.e. to the ACR value of test-pieces.

Simultaneously, as the number of cracks increased, the sulfur content of test-pieces increased from 0.2% to 2.1-4.8%. It was assumed that during base-catalyzed elimination of hydrofluoric acid caused by basic dispersants, revulcanization took place on the surfaces in the presence of sulfur containing engine oil compounds (base oil molecules, detergent and antiwear additives).

Brighter spots in the ESEM pictures derived from heavier elements such as inorganic fillers and additives in fluoroelastomer (Ca, Mg, Ti and Zn compounds). In Figure 5 it can be seen that after immersion and having serious cracks the number of these brighter spots decreased and also the concentration of fillers (3.6-3.0%) decreased (Table 7). It was assumed that the evolved hydrofluoric acid formed metal-fluorides from fillers and additives, and these compounds were removed and dissolved into the engine oil[7].

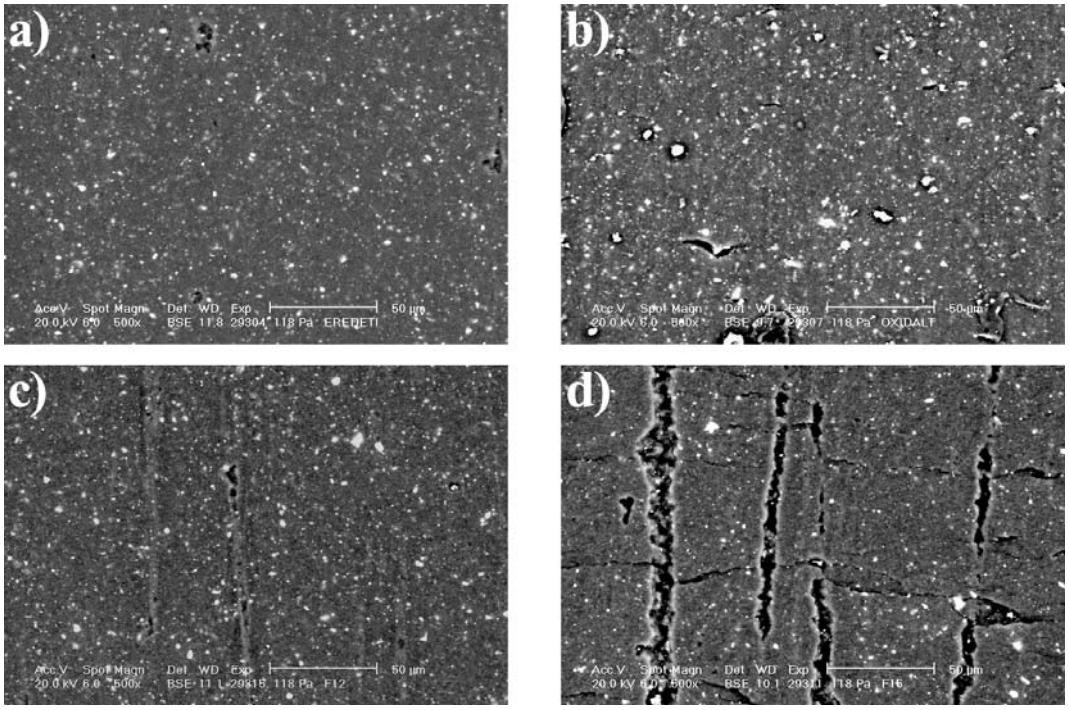

Figure 5 Surfaces of different test-pieces: a) original S3A, b) pre-aged, c) no cracks, d) seriously cracked (ESEM 500x magn.)

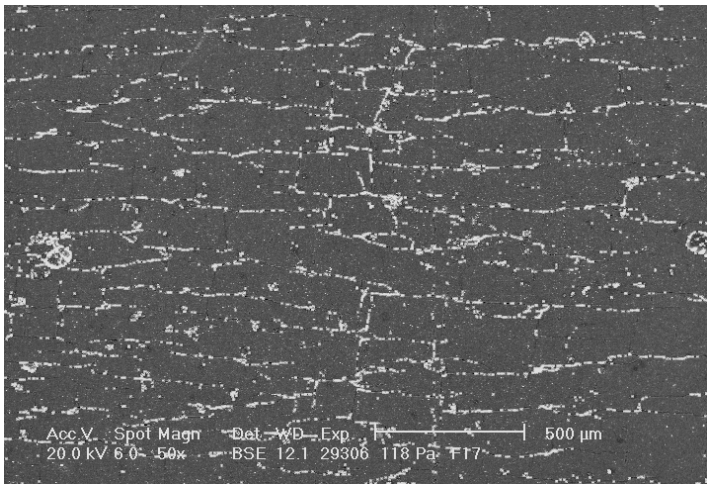

Figure 6 Seriously cracked test-piece of M1 sample (ESEM, 50x magnification),using Adobe Photoshop CS2 the cracks were highlighted by white colour.

Table 7 Elemental composition of the surface of test-pieces (ESEM-EDAX)

Sample	ACR, %	Cracks	C, %	O, %	S, %	F, %	Fillers and additives, %
Original S3A	100	no	49.60	2.33	0.16	44.28	3.62
Pre-aged S3A	100	no	50.40	2.62	0.26	43.11	3.61
M14	100	no	51.18	3.43	0.18	41.74	3.47
M15	100	no	50.96	3.56	0.17	41.71	3.61
M16	100	no	51.91	3.11	0.17	41.13	3.68
M17	100	no	52.57	2.49	0.99	40.40	3.55
M8	99.72	little	55.90	3.50	2.09	35.03	3.48
M4	95.10	many	60.26	4.40	3.09	28.95	3.30
M1	92.22	serious	60.97	5.15	4.82	26.06	3.00

4. CONCLUSION

During the investigation of engine oil fluoroelastomer compatibility according to VW PV 3344 standard it was concluded that our method fulfilled the precision requirements of DIN 53504 tensile test standard. The visual evaluation of cracks on surfaces of test-pieces was developed by a new method based on photography and digital image processing. Using the so called Area Covering Ratio (ACR) four statistically different (at 99 or 99.97% probability level) categories could be established in case of cracked fluoroelastomer. On the whole, a simple, quick, reliable and cheap method was developed which resulted in better ability for differentiation among similar engine oils and additives in seal compatibility tests. Even if the pre-ageing itself did not alter significantly the mechanical properties of test-pieces, ESEM-EDAX investigations proved that after pre-ageing of specimens small cracks could be observed on the surfaces. Test-pieces which were seriously attacked after immersion into engine oils showed huge, 300-800 μm length cracks.

ESEM-EDAX elemental analyses proved that the number of cracks and ACR values correlated to the fluorine content, as it was expected, as a proof of base-catalyzed elimination of hydrofluoric acid. As the cracks on the surfaces increased the fluorine contents of test-pieces strongly decreased while the metal contents (fillers and additives of elastomer) slightly decreased. On the surface of seriously cracked fluoroelastomer revulcanization could take place with the sulfur compounds of engine oils which resulted in increasing sulfur contents of test-pieces.

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