International Journal of
Chemical, Environmental and Pharmaceutical Research

Vol. 2, No.1, 12-19
January-April, 2011

Chemical Analysis on Different Oils Use in Tyre Tread Cap Compound

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Article History:
Received: 17 March 2011
Accepted:23 March 2011

ABSTRACT

The global market place is increasingly demanding safe process oils to reduce the environmental impact of tires. The replacement of classified distillate aromatic extracts by non-carcinogenic MES, TDAE, or naphthenic process oils will reduce the PAH emissions. . In the present work three types of low PCA and one regular high PCA Petroleum oils were chemically analyzed. The oils were characterized for different chemical analysis . These low PCA oils can act as the best alternative processing aids for rubber industry. The rheological, properties of SSBR loaded with different LPCA & HPCA oils have been studied. in order to obtain similar properties. The data show that the best results are obtained using LPCA. A comparative study has been carried out on SSBR filled with various oils.

Key words: low PCA oils, Polycyclic aromatics, carcinogenesis, PAH, risk assessment.

INTRODUCTION

In compounding rubber and rubber composition for use in pneumatic tyre, it is common to utilize processing oils to soften and extend the rubber[7]. Typical, aromatic processing oils, having a certain content of poly aromatic compound or polyaromatic hydrocarbons ,have bee used .recently , regulatory concerns have necessisted the use of processing oils having alower PCA content.

Rubber formulations used in various tyre components previously have been designed using conventional processing oils .How ever, in changing to the use of the lower PCA content oils ,some lose in rubber compound performance is noted. It is , there for necessary to develop new rubber compounds that provide desirable performance levels wile in corporating the use low PCA oils[8].

EXPERIMENTAL

Materials studied are given in Table 1.

Physicochemical characterization

The oils were characterized for Specific gravity by hydrometer (ASTM D 1298) , flash and fire point (ASTM D92), pour point (ASTM D97), specific gravity (ASTM D1298), saybolt viscosity (ASTM D88), Fourier transform infrared (FTIR) spectroscopic study of the petroleum oils was performed in a FTIR System from PERKIN ELMER, USA for checking functional groups present[1-3].

Compound mixing

Mixing of rubber compound was carried out using a two-wing rotor laboratory Banbury mixer (Stewart Bolling, USA) in three stages (master batch remill and final batch) and the formulations are given in Table

Master batch mixing was done setting the temperature control unit (TCU) at 90°C and rotor speed at 60 rpm.. After the power integrator (PI) indicated achievement of 0.32 kWh, the master batch was dumped. The dump temperature of the master batches was found to be within 140 - 150°C. The master batches were sheeted out in a laboratory two-roll mill. Further mixing of the master batches were carried out after a maturing period of 8 hours[8].

For final batch mixing, the TCU was kept at 60^0C and rotor speed at 30 rpm. The earlier prepared master batch was mixed with sulfur, accelerator and scorch inhibitor. The batch was dumped at a PI reading of 0.12 kWh. The dump temperature of the batches was found to be within 95 – 105°C. The final batches were also sheeted out on a laboratory two-roll mill[8-12] Formulation is according to Table 2.

Table-1: Material Required

1	S SBR having regular aromatic oil
2	S SBR having low PCA oil (3830)
3	Regular oil and LPCA OIL No.1,2,3,
4	Filler N339 black
5	ZnO
6	Stearic Acid
7	6PPD
8	MC Wax
9	MS 40
10	S
11	TBBS
12	DCBS
13	PVI

RESULTS AND DISCUSSION

1. Flash and Fire Point

The flash point of a volatile liquid is the lowest temperature at which it can vaporize to form an ignitable mixture in air**.** Measuring a liquid's flash point requires an ignition source. At the flash point, the vapor may cease to burn when the source of ignition is removed. The flash point is not to be confused with the autoignition temperature**,** which does not require an ignition source. The fire point, a higher temperature, is defined as the temperature at which the vapor continues to burn after being ignited. Neither the flash point nor the fire point is related to the temperature of the ignition source or of the burning liquid, which are much higher.

The flash point is often used as a descriptive characteristic of liquid fuel**,** and it is also used to help characterize the fire hazards of liquids. "Flash point" refers to both flammable liquids and combustible liquids. There are various standards for defining each term. The flash and fire point results are shown in Table 3.

Flash and fire point is one of the important criteria for determining the process safety while handling the rubber compound during mixing, calendaring, extrusion etc. Higher flash and fire point of oils always indicates good process safety. High flash and fire point of oils may be due to presence of carbonyl groups, alkaloids groups etc[11].

2. Pour Point

The pour point of a liquid is the lowest temperature at which it will pour or flow under prescribed conditions. It is a rough indication of the lowest temperature at which oil is readily pumpable.

Also, the pour point can be defined as the minimum temperature of a liquid, particularly a lubricant, after which, on decreasing the temperature, the liquid ceases to flow.The pour point results are shown in Table 4. All the Low PCA oils show pour point less than 0°C except aromatic oil. Lower pour point improves the handling of oils during winter season. Surrounding temperature during winter season reduces drastically when some processing oils require heating arrangement for ease of flow to the Banbury chamber for mixing. Additional energy consumption is required for such heating process. With natural oils, such additional processing costs can be eliminated.

3. Saybolt viscosity

Viscosity describes a fluid's internal resistance to flow and may be thought of as a measure of fluid friction**.** For example, high-viscosity felsic magma will create a tall, steep stratovolcano, because it cannot flow far before it cools, while low-viscosity mafic lava will create a wide, shallow-sloped shield volcano**.** All real fluids (except superfluids) have some resistance to stress and therefore are viscous, but a fluid which has no resistance to shear stress is known as an ideal fluid or inviscid fluid.

The study of flowing matter is known as rheology, which includes viscosity and related concepts.The saybolt viscosity results are shown in Table 5. High Saybolt viscosity indicates higher aromaticity.

4. Aniline Point

Aniline point is defined as the temperature at which equal volumes of aniline($C_6H_5NH_2$) and diesel oil are completely miscible**.** The value gives an indication of the aromatic content of diesel oil, since aniline is an aromatic compound which is dissolved on heating by the aromatics in diesel oil. The greater the aniline point, the lower the aromatics in diesel oil. A higher aniline point also indicates a higher proportion of paraffin**.** The diesel index is directly related to aniline point as:

DIESEL INDEX = ((ANILINE POINT(DEG F))(API GRAVITY))/100

A higher aniline point (and therefore a lower aromatic content) in diesel oil is desirable, in order to prevent autoignition in diesel engines.In cases where the Aromatic content in the oil is very high, in such cases "Mixed Aniline Point" needs to me measured to determine the approximate content of Aromatic in the oil.The aniline point results are shown in Table 6.

All the Low PCA oils show higher values whereas High PCA oils show lower values. Aniline point indicates the presence of aromatic ring in the oils. Higher the aromatic groups lower the aniline point.

5. Specific gravity

Specific gravity is the heaviness of a substance compared to that of water, and it is expressed without units. In the metric system specific gravity is the same as in the English system[10].

In relationship to liquids, the term specific gravity is used to describe the weight or density of a liquid compared to an equal volume of fresh water at 4°C (39° F). If the liquid you are comparing will float on this water it has a specific gravity of less than one. If it sinks into the fresh water the specific gravity is more than one. As you have already guessed fresh water at 4°C (39° F) has been assigned a value of one. The specific gravity results are shown in Table 7.

6. Aromatic content (C_A)

The aromatic content results are shown in Table 8.Higher aromatic content is basically the presence of polycyclic group in the oils.

7. FTIR Study for surface group

IR bands of aromatic C-H stretching at 3010 and 3080 cm^{-1} and overtone and combination band due to C-H out-of-plane at 1600-2000 cm^{-1} were observed. Also, IR band of aromatic ring CC stretching and aromatic C-H in-plane appeared in 1000-1200 cm^{-1} region[9].The FTIR results are shown in Table 9.

CONCLUSION

The recent change in world scenario in shifting towards low PCA oils and restriction on high PCA oils. Present study is focused on chemical, analytical and compound characterization of petroleum oils. These oils were found to be suitable on the basis of low PCA content.. All non-carcinogenic process oils contain very low concentrations of polycyclic aromatic hydrocarbons and meet the 1 mg/kg benzo[a]pyrene limit set by the VDA. Hence, the replacement of HPCA by non-carcinogenic process oils in oil extended natural or synthetic rubber and therefore in finished tires will reduce the PAH emission from tire wear by more than 98 %. Test results are intended to support the rubber and tire industries in their environmental challenge to replace the classified aromatic oils. Further extensive compounding and evaluation work will be required by each company using its proprietary tire formulation technology. Demand for these oils is expected to rise as car manufacturers realise that carcinogenic emissions from tires can hereby be greatly reduced. It has demonstrated on a commercial scale that this challenge can be met by a change to safer alternatives such as LPCA . The production LPCA oil are already on the market[12].

ACKNOWLEDGEMENTS

The author would like to thank IIT Kharagpur (W.B.) & J K Tyre HASETRI Kankroli, Rajasthan for excellent cooperation, extensive evaluations and discussion.

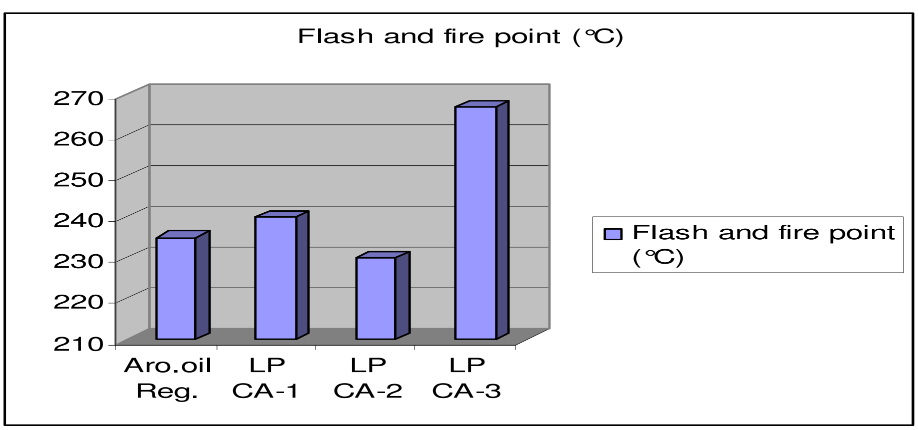

Fig.-1: Flash and fire point

Table-2: Formulation

Ingredients	HPCA	LPCA-1	LPCA-2	LPCA-3
RMA4	27	27	27	27
BR	35	35	35	35
VSL5525	52	--	--	--
Tufden3830	--	52	52	52
N339	60	60	60	60
Reg Ar. Oil	5	--	--	--
LPCA-1	--	5	--	--
LPCA-2	--	--	5	--
LPCA-3	--	--	--	5
ZnO(WS)	2.25	2.25	2.25	2.25
St Acid	0.5	0.5	0.5	0.5
6PPD	1.9	1.9	1.9	1.9
MC Wax	2.4	2.4	2.4	2.4
MS 40	1	1	1	1
S(108)	2.2	2.2	2.2	2.2
TBBS	1.2	1.2	1.2	1.2
DCBS	0.6	0.6	0.6	0.6
PVI	0.15	0.15	0.15	0.15
Batch weight	191.2	191.2	191.2	191.2

Table-3: : Flash and fire point

Name of oils	Flash and fire point(°C)
Aromatic oil regular	235
Low PCA oil No.1	240
Low PCA oil No.2	230
Low PCA oil No.3	267

Table-4: Pour point

Name of oils	Pour point (°C)
Aromatic oil regular	7
Low PCA oil No.1	-8
Low PCA oil No.2	4
Low PCA oil No.3	-4

Table-5: Saybolt viscosity

Name of oils	Saybolt viscosity(sec)
Aromatic oil regular	130
Low PCA oil No.1	105
Low PCA oil No.2	65
Low PCA oil No.3	120

Table-6: Aniline point

Name of oils	Aniline point (°C)
Aromatic oil regular	46.5
Low PCA oil No.1	100
Low PCA oil No.2	30
Low PCA oil No.3	105

Table -7: Specific gravity

Name of oils	Specific gravity
Aromatic oil regular	1.001
Low PCA oil No.1	0.916
Low PCA oil No.2	0.938
Low PCA oil No.3	0.921

Table -8: Aromatic content

S.No.	Carbon type analysis (%)	Low PCA 1	Low PCA 2	Low PCA 3	Aromatic oil
1	CA	19.8	-	16.1	36.8
2	CP	59.8	-	68.4	58.7
3	C N	20.4	-	15.5	4.5

Table-9: FTIR study

Name of oils	Surface group present
Aromatic oil regular	Alkyl group $–CH_2$-R St. Aromatic substituent C-H St.
Low PCA oil No.1	Alkyl group CH_2-R St. Alkyl group CH_2-R St. Aromatic substituent C-H St.
Low PCA oil No.2	Aliphatic hydrocarbon C-H St. Aliphatic hydrocarbon $–CH_2$-R St. Aromatic substituent C-H St
Low PCA oil No.3	Aliphatic hydrocarbon St. Aliphatic hydrocarbon (Short chain compound or substituent)

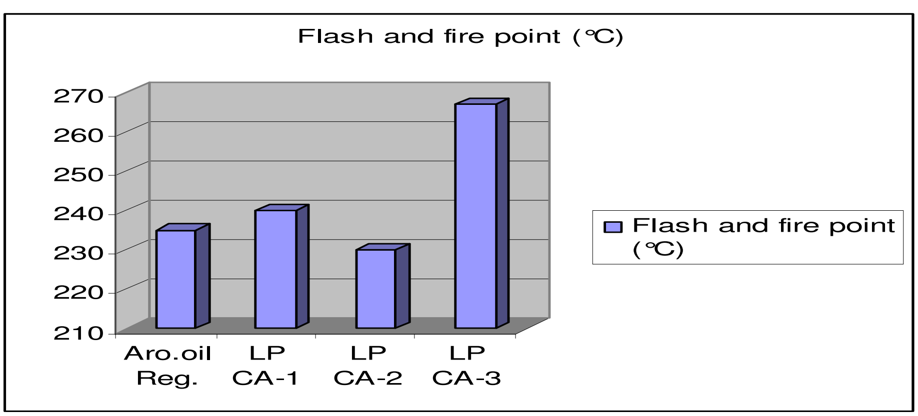

Fig.-2: Flash and fire point

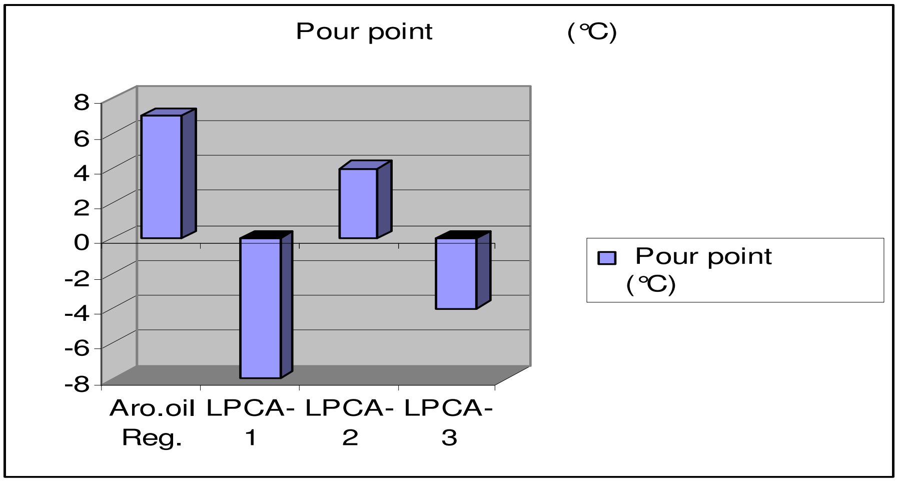

Fig.-3: Pour point

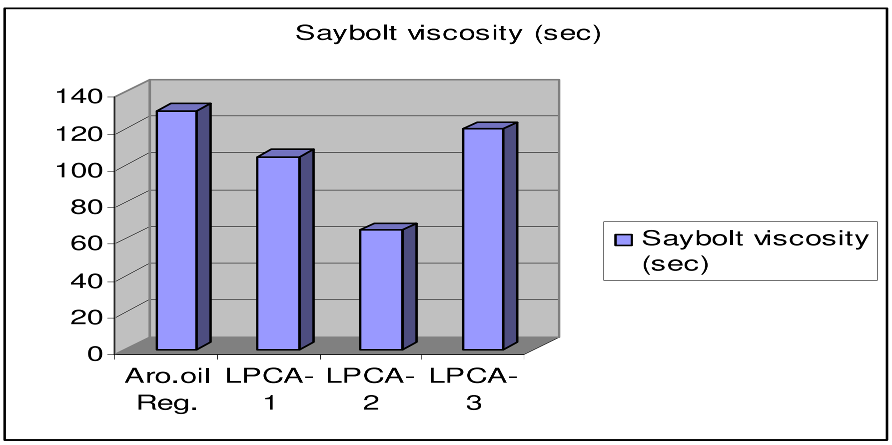

Fig.-4: Saybolt viscosity

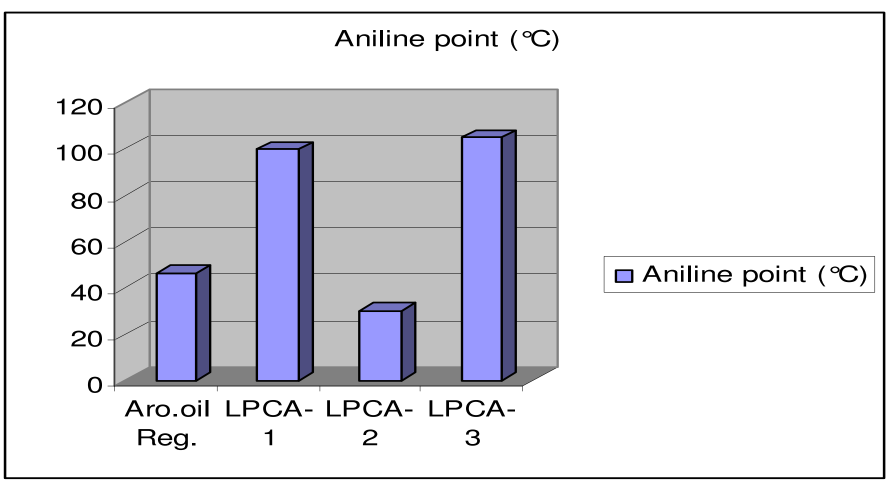

Fig.-5: Aniline point

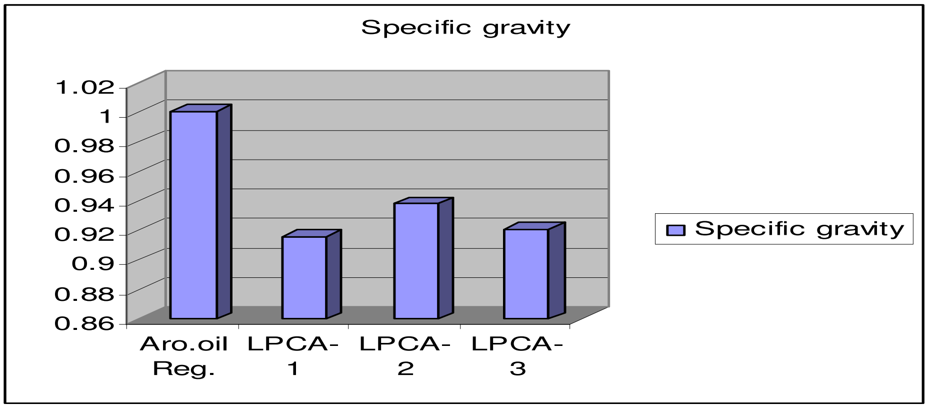

Fig.-6: The specific gravity

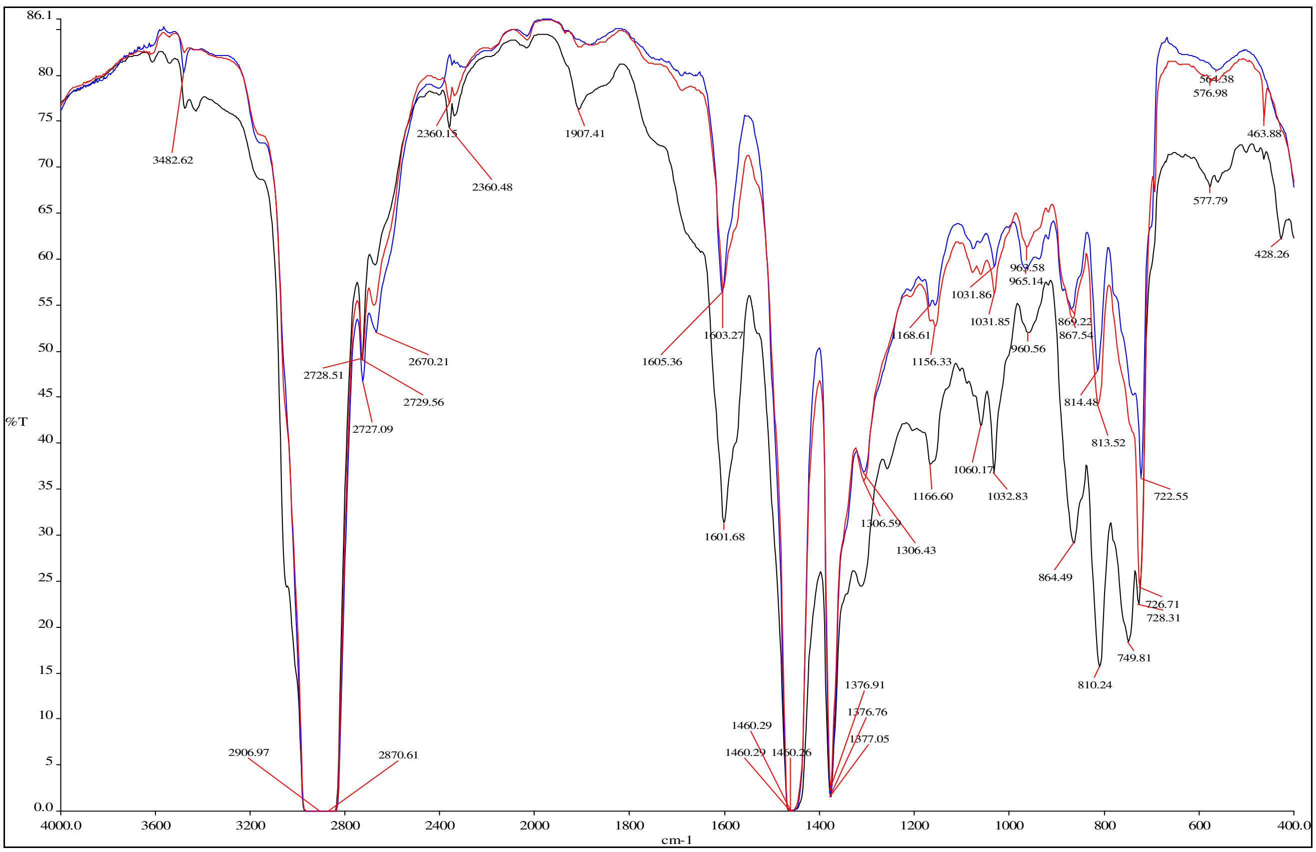

Fig.-7: FTIR of oils: Black color high PCA/ Blue color Oil No1/ Red color Oil 2

Table-10: Rheometric Properties @ 193^{0}C/2.5min

TEST	HPCA	LPCA-1	LPCA-2	LPCA-3
tS2 (min)	0.66	0.64	0.64	0.63
tC10 (min)	0.53	0.51	0.52	0.5
MIN TQ. (lb-in)	0.23	0.23	0.22	0.22
tC40 (min)	0.83	0.8	0.81	0.8
MAX.TQ.(lb-in)	1.19	1.84	1.87	1.82
tC50 (min)	0.88	0.84	0.86	0.84
Final TQIlb-in)	13.61	13.18	13.06	13.26
tC90 (min)	1.19	1.15	1.17	1.14
tS1 (min)	0.49	0.49	0.5	0.48

Table-11: Rheometric Properties @ 160 C/30min (Final)

TEST	HPCA	LPCA-1	LPCA-2	LPCA-3
MIN TQ. (lb-in)	2.45	2.67	2.64	2.76
MAX.TQ.(lb-in)	15.84	15.76	15.4	16.09
Final TQ.(Ilb-in)	14.56	14.21	13.88	14.57
tS1 (min)	4.1	4.09	4	4.22
tS2 (min)	5.07	4.94	4.74	5.08
tC10 (min)	4.59	4.47	4.32	4.64
tC40 (min)	5.69	5.58	5.38	5.77
tC50 (min)	5.87	5.77	5.59	5.97
tC90 (min)	7.79	7.66	7.57	7.85
Max-Min Tq.(lb-in)	13.39	13.09	12.76	13.33

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