Research Article

Stefan Ptak*, Wojciech Krasodonski, Janusz Jakóbiec, Artur Antosz

Modified TDAE petroleum plasticiser

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Abstract: Petroleum plasticisers are applied as softening additives in rubber vulcanisation processes and as components of rubber mixtures in the production and vulcanisation process. They contain polycyclic aromatic compounds exhibiting carcinogenic and mutagenic effects. Since 2010, the European Union has banned the use of high-aromatic DAE plasticisers. The petroleum industry and tyre manufacturers are developing new types of petroleum plasticisers. The best alternative to the DAE is the TDAE plasticisers, obtained mainly by selective solvent refining. The solvent dewaxing process of classic TDAE plasticisers was studied in order to improve the chemical composition as well as the rheological and low-temperature properties of deparaffinate. This article presents the results of an examination of the TDAE plasticiser samples subjected to solvent dewaxing process on a laboratory scale with three types of solvents, MEK–TOL, MEK–MIBK and MEK–MTBE. It was demonstrated that solvent dewaxing of the TDAE plasticiser with positive pour points maintains good process selectivity and allows for a significant reduction of the plasticiser pour point, thus improving the rheological and low-temperature properties. In all dewaxing attempts, the pour point in the deparaffinate decreased significantly to the range –12 to –22°C, compared to the positive pour points of the raw materials. The application tests for two types of the TDAE plasticisers, used to produce oiled rubber and a standard rubber compound, meet the quality requirements for those products.

Keywords: petroleum plasticisers, TDAE plasticisers, solvent dewaxing, polycyclic aromatic hydrocarbons, rubber mixtures

1 Introduction

Petroleum plasticisers are applied as softening additives in rubber vulcanisation processes, in particular for the synthetic styrene–butadiene rubber (SBR), and as components of rubber mixtures in the production and vulcanisation processes. The global elastomer market is dominated by two types of rubbers, namely the natural rubber and SBR, which account for 70–75% of the global elastomer market segment, especially in applications such as car tyres including treads [1]. The annual demand for petroleum plasticisers in 2010 [2] was 1.3 million tons (Figure 1).

Petroleum plasticisers for the rubber industry are required to meet a number of requirements arising from the specific nature of manufacturing processes and operating conditions of rubber products, which are in particular:

- to have the chemical composition required for a given application and have appropriate physiochemical properties;
- show sufficient compatibility with the rubber used;
- exhibit low volatility in the rubber production process conditions and in production and vulcanisation of rubber mixtures;
- have no toxic effects [3], especially no carcinogenic effect [4–7].

Petroleum plasticisers are classed as petroleum agents [8] used in the production of rubber and gum products. As a rule, the plasticiser used in SBR rubber compositions is referred to as filler oil, which consists of hydrocarbon molecules containing 25–35 carbon atoms.

Petroleum plasticisers are divided into aromatic, naphthenic, and paraffinic ones, depending on the percentage of carbon in aromatic, naphthenic, and paraffinic structures [9].

One of the petroleum plasticiser classifications is based mainly on the methods of production. It distinguishes the following types of plasticisers [10,11]:

- DAE (distillate aromatic extract) – an aromatic extract obtained from a petroleum vacuum distillate. It has been in use by tyre manufacturers for a long time because of the low cost and high compatibility with SBR rubber [12–16].

* **Corresponding author: Stefan Ptak**, Oil and Gas Institute – National Research Institute, Lubicz 25A, 31-503 Kraków, Poland, e-mail: ptak@inig.pl

Wojciech Krasodonski, Artur Antosz: Oil and Gas Institute – National Research Institute, Lubicz 25A, 31-503 Kraków, Poland

Janusz Jakóbiec: State Higher Vocational School in Nowy Sącz, Pl. S. Staszica 1, 33–300 Nowy Sącz, Poland

Figure 1: Global, annual demand for petroleum plasticisers as per regions of the world.

- TDAE (treated distillate aromatic extract) – a modified aromatic extract from a petroleum vacuum distillate;
- MES (mild extraction solvates) – raffinate of mild solvent extraction of petroleum vacuum distillate;
- RAE (residual aromatic extract) – an aromatic extract obtained from DAO (Deasphaltisate) in the production of Brighstock;
- TRAE (residual aromatic extract) – a modified aromatic extract obtained from DAO in the production of Brighstock;
- NAP (naphthenic plasticisers) – raffinate from solvent extraction of vacuum distillate from naphthenic oil, which is further broken down into
 - LNAP – naphthenic plasticisers of medium viscosity;
 - HNAP – naphthenic plasticisers of high viscosity.

From early 2010, a ban on the use of high aromatic plasticisers [7] was introduced, which challenged the oil and tyre industry to replace the DAE high aromatic plasticisers with other process oils.

Patent application EP 3031621 A1 [17] of The Goodyear Tire & Rubber Company; PNEUMATIC TIRE, describes the production of a pneumatic tyre based on oiled rubber compositions and addition of process oil directly when composing the rubber mixture.

Plasticisers of the type MES, TDAE and naphthenic oils are used in the solutions of the said invention, thus the rubber composition contains low polycyclic aromatic compounds (PAC) plasticisers so they do not show carcinogenic activity.

The MES, TDAE or naphthenic type plasticisers with general qualitative characteristics are shown in Table 1.

Petroleum plasticisers are important components of rubber products and have a significant impact on their performance characteristics [18]. The function of mineral softeners involves, among others, modification of the physical properties of rubber, particularly by improving tensile strength, hardness, tear resistance and elasticity at low temperatures [18]. The above-mentioned impact of petroleum plasticisers on the performance characteristics of rubber products at low temperatures and an attempt to improve the structural composition of hydrocarbons was an inspiration to study the dewaxing process of the classic TDAE plasticiser.

As a result of the solutions described in numerous patents [19–29], the product obtained is a process oil containing PAC of $\leq 3\%$ (m/m), which can be used as a softener or plasticiser for rubbers and their mixtures.

The TDAE petroleum plasticisers offered by many producers are distinguished by a plus pour point, which is a feature that can adversely affect the elasticity of

Table 1: Physiochemical properties of petroleum plasticisers

Properties	MES	TDAE	Heavy naphthenic (HNAP)
Content of carbon atoms in structures: C_A , %	11–17	25–30	11–17
Density at 15°C, g/cm ³	0.895–0.925	0.930–0.960	0.920–0.950
Viscosity at 40°C, mm ² /s	150–230	370–430	350–720
Viscosity at 100°C, mm ² /s	13–17	16–22	17–33
VGC viscosity and density constant	0.825–0.865	0.860–0.890	0.840–0.870
Intercept fractions	1.495–1.510	1.520–1.540	1.500–1.520
Glass transition temperature, T_g , °C	–60 ± 3	–47 ± 3	–45 ± 3
Aniline point, °C	85–100	—	—
Solidification point, °C	<0	<30	<0
PAC content (DMSO extr.), % (m/m)	<2.9	<2.9	<2.9
Flash point, (to) °C	220	240	240

rubber products at low temperatures, and hence, in case of a positive effect of the dewaxing process, a decrease in the pour point of those plasticisers can be expected and their performance at low temperatures can be improved.

2 Experimental

2.1 Materials for testing the solvent dewaxing process

Heavy extracts from a selective solvent refining plant were the raw materials for obtaining TDAE plasticisers by the dewaxing process with furfural (classic process). The physiochemical properties of heavy extracts are presented in Table 2, and the samples of obtained plasticisers TDAE I–III are given in Table 3.

2.2 Laboratory solvent dewaxing process method

Crystallisation of solid hydrocarbons under laboratory conditions is effected with the aid of the method of gradual cooling of the oil–solvent mixture located in the crystalliser.

The crystalliser is placed in a cooling bath equipped with a cooling cycle controller to set up the final crystallisation temperature and appropriate cooling rates in the subsequent stages of the process. A nutch filter is connected to a cryostat, provided with a jacket in which the coolant circulates.

The crystallisation process is effected by the dilution method by adding successive portions of the cooled solvent to the cooled mixture of the raw material and solvent, at appropriate moments of the cooling cycle. The first portion of solvent is introduced into the raw material at a temperature at which the raw material forms a homogeneous liquid phase containing no crystals. However, at the point of injection into the mixture, the temperature of the solvent has to be such as to prevent disturbance of the hydrocarbon crystallisation process in the mixture.

In the crystallisation process, continuous mixing of the crystalliser content is effected by means of an agitator with an anchoring ending, with the mixing speed adapted to the increasing viscosity of the mixture.

After reaching the final crystallisation temperature, the separated solid hydrocarbons, containing the occluded solvent, are filtered out from the oil solution in a vacuum nutch. The oil solution (filtrate) accumulates in the receiver tank. The filtered solid hydrocarbons are washed with a portion of cold solvent. The solid hydrocarbons collected from the nutch and the filtrate are subjected to the solvent

Table 2: Physiochemical properties of raw materials (heavy extracts)

Properties	Raw material			Test methods
	Extract I	Extract II	Extract III	
Density at 20°C, g/cm ³	0.9749	0.9893	0.9916	PN-EN ISO 12185
Kinematic viscosity at 50°C, mm ² /s	275.43	739.31	783.53	PN-EN ISO 3104
Flash point, (to), °C	275	279	281	PN-EN ISO 2592
Refractive index n_D^{20}	1.5547	1.5614	1.5648	PN-C-04952:81
Sulphur content, % (m/m)	2.76	3.22	3.35	PN-EN ISO 8754
Pour point, °C	+29	+26	+25	PN-ISO 3016
PAC content (DMSO extr.), % (m/m)	13.6	12.8	13.0	IP 346
Content of carbon atoms in structures				ASTM D 2140
Aromatic, C _A , %	34.51	35.33	36.85	
Naphthenic, C _N , %	11.83	15.04	12.29	
Paraffinic C _P , %	53.66	49.63	50.86	
PAH content, mg/kg				Met. GC/MS
Benzo(a)pyrene	9.4	7.3	6.8	
Benzo(e)pyrene	26.8	25.8	24.9	
Benzo(a)anthracene	5.3	2.4	2.3	
Chrysene	28.5	27.4	18.7	
Benzo(b,j,k)fluoranthene	24.2	14.7	14.3	
Dibenzo(a,h)anthracene	3.5	2.3	1.8	
Total PAHs	97.7	79.9	68.8	

Table 3: Physiochemical properties of TDAE plasticisers

Properties	Plasticiser			Test methods
	TDAE I	TDAE II	TDAE III	
Density at 20°C, g/cm ³	0.9398	0.9478	0.9541	PN-EN ISO 12185
Kinematic viscosity at 100°C, mm ² /s	15.33	22.29	24.47	PN-EN ISO 3104
Flash point, (to), °C		276	271	PN-EN ISO 2592
Refractive index n_D^{20}	1.5223	1.5302	1.5349	PN-C-04952:81
Sulphur content, % (m/m)	2.5356	2.68	3.04	PN-EN ISO 8754
Pour point, °C	+33	+30	+28	PN-ISO 3016
PAC content (DMSO extr.), % (m/m)	2.7	1.9	2.4	IP 346
Content of carbon atoms in structures				ASTM D 2140
Aromatic, C _A , %	20.3	23.86	25.84	
Naphthenic, C _N , %	24.2	19.14	16.49	
Paraffinic C _P , %	55.5	56.99	57.67	
PAH content, mg/kg				Met. GC/MS
Benzo(a)pyrene	0.8	0.7	0.7	
Benzo(e)pyrene	3.1	0.9	0.9	
Benzo(a)anthracene	0.3	0.3	0.4	
Chrysene	1.3	1.1	1.2	
Benzo(b,j,k)fluoranthene	1.4	1.2	1.4	
Dibenzo(a,h)anthracene	0.4	0.1	0.1	
Total PAHs	7.3	4.2	4.7	

Table 4: Technology parameters, mass balance and properties of the obtained deparaffinates and slack waxes, in MET-TOL dewaxing processes of TDAE I and TDAE III raw material samples

Dewaxing no.	PR 01	PR 02	PR 03	PR 04	PR19
Raw material, sample no.	TDAE I	TDAE I	TDAE I	TDAE I	TDAE III
Technology parameters of dewaxing processes					
MEK-TOL solvent, weight ratio	40:60	40:60	60:40	70:30	50:50
Crystallisation/filtration temperature, °C	−28	−20	−28	−28	−28
Total solvent to fraction ratio	11:1	11:1	5.0:1	5.0:1	5.0:1
Mass balance of dewaxing processes, averaged results					
Filtration time, s	35	18	14.5	27	19
Deparaffinate yield, % (m/m)	88.0	91.0	89.0	90.0	89.0
Slack wax yield, % (m/m)	9.0	7.0	6.0	7.0	8.0
Losses, % (m/m)	3.0	2.0	5.0	3.0	4.0
Properties of deparaffinate					
Kinematic viscosity at 50°C, mm ² /s	152.9	138.4	156.3	153.4	289.3
Kinematic viscosity at 100°C, mm ² /s	16.49	15.68	16.58	16.78	24.17
Refractive index n_D^{20}	1.5253	1.5245	1.5256	1.5258	1.5330
Density at 20°C, g/cm ³	0.9424	0.9408	0.9411	0.9415	0.9563
Sulphur content, % (m/m)	2.97	3.10	3.10	3.09	3.11
PAC content (DMSO extr.), % (m/m)	—	2.8	2.8	2.8	2.1
Content of carbon atoms in structures					
Aromatic, C _A , %	21.28	20.99	21.51	21.73	24.09
Naphthenic, C _N , %	20.61	19.87	19.98	19.42	18.41
Paraffinic C _P , %	58.11	59.14	58.51	58.85	57.50
Pour point, °C	−15	−15	−22	−14	−15
Slack wax properties					
Refractive index n_D^{70}	1.4705	1.4702	1.4639	1.4687	1.4722
Solidification point, °C	55.0	60.0	54.8	55.9	56.2
Oil content, % (m/m)	50.65	0.73	15.60	24.27	28.2

regeneration process. The solvent regeneration operation is performed by means of nitrogen stripping distillation.

2.3 Solvent dewaxing processes with various TDAE plasticiser solvents

Samples of TDAE plasticisers were subjected to a solvent dewaxing process with three different types of solvents, MEK–TOL (methyl ethyl ketone/toluene mixture), MEK–

MIBK (methyl ethyl ketone/methyl isobutyl ketone mixture) and MEK–MTBE (methyl ethyl ketone/methyl *tert*-butyl ether). To perform solvent dewaxing processes in a laboratory system, similar technology parameters were adopted as those of industrial plants and described in patents [30–33].

The technology parameters applied are presented in the tables together with mass balances and properties of the deparaffinates obtained and slacks from dewaxing processes. The initial charge of the vacuum distillate in the dewaxing process was 300 g for all the tests carried

Figure 2: Effects of the dewaxing process with the MEK–TOL solvent on the change of the structural composition of deparaffinates – TDAE I raw material.

Figure 3: Effect of the dewaxing process with the MEK–TOL solvent on the change of the deparaffinate pour point – TDAE I raw material.

out. The crystallisation modifier (VISCOPLEX 9-350) was dosed at 1,000 mg/kg according to the manufacturer's instructions.

3 Results and discussion

3.1 Dewaxing the TDAE plasticiser with the MEK–TOL solvent

Table 4 presents technology parameters, mass balance and properties of the obtained deparaffinates and slack waxes, for four MET-TOL dewaxing processes of TDAE I and TDAE III raw material samples.

The basic process parameters for four dewaxing operations of the TDAE I raw material were as follows: the mass ratio of MEK–TOL was in the range from 40:60 to 70:30, the

crystallisation temperature was -20 or -28°C , and the total solvent to fraction ratio was from 5.0:1 to 11:1.

In the dewaxing attempts of the TDAE I raw material, the deparaffinate yield was large and ranged from 88.0 to 91.0% (m/m) and the slack wax yield was in the range of 6.0–9.0% (m/m).

Compared to the TDAE I raw material, as a result of the dewaxing process in the TDAE deparaffinate, an increase in the carbon content in aromatic structures in deparaffinate was observed for all tests, which ranged from 0.69 to 1.43%; the content of carbon atoms in naphthenic structures decreased to 3.59–4.78%; and the content of carbon atoms in paraffin structures increased from 2.61 to 3.64%.

It has to be stressed that in all dewaxing attempts, the pour point in the deparaffinate decreased significantly in the range of -14 to -22°C , compared to the raw material whose pour point was $+33^{\circ}\text{C}$.

Compared to deparaffinates and raw material in slack waxes, the refractive index markedly decreased and the

Table 5: Technology parameters, mass balance and properties of the obtained deparaffinates and slack waxes, in MIBK–MEK dewaxing processes of TDAE II and TDAE III raw material samples

Dewaxing no.	PR 05	PR 06	PR 07	PR 08	PR 09	PR 10	PR 11
Raw material, sample no.	TDAE II	TDAE II	TDAE II	TDAE II	TDAE II	TDAE III	TDAE III
Viscosity modifier	—	Viscoplex 9–350	—	—	—	—	Viscoplex 9–350
Technology parameters of dewaxing processes							
MIBK–MEK solvent, mass ratio	100:0	60: 40	80: 20	60: 40	50: 50	60: 40	40: 60
Crystallisation/filtration temperature, $^{\circ}\text{C}$	-28	-28	-28	-20	-20	-28	-20
Total solvent to fraction ratio	5.0: 1	5.0: 1	7: 1	5.7: 1	3.5: 1	5.5: 1	3.5: 1
Mass balance of dewaxing processes, averaged results							
Filtration time, s	112	208	62	87	94	54	72
Deparaffinate yield, % (m/m)	87.0	88.0	86.0	89.0	91.0	91.0	92.0
Slack wax yield, % (m/m)	10.0	7.0	11.0	9.0	6.0	7.0	5.0
Losses, % (m/m)	3.0	5.0	3.0	2.0	3.0	2.0	3.0
Properties of deparaffinate							
Kinematic viscosity at 50°C , mm^2/s	313.8	258.8	294.7	318.9	297.4	323.4	318.2
Kinematic viscosity at 100°C , mm^2/s	25.24	23.09	24.63	25.67	24.93	27.83	27.48
Refractive index n_D^{20}	1.5134	1.5338	1.5338	1.5334	1.5336	1.5387	1.5184
Density at 20°C , g/cm^3	0.9525	0.9529	0.9564	0.9564	0.9552	0.9527	0.9526
Sulphur content, % (m/m)	2.78	2.77	3.16	3.19	3.18	3.3	3.20
PAC content (DMSO extr.), % (m/m)	2.1	2.1	2.2	2.2	2.2	2.7	2.7
Content of carbon atoms in structures							
Aromatic, C_A , %	25.27	24.98	24.93	24.98	25.18	26.81	26.43
Naphthenic, C_N , %	18.89	18.45	18.79	19.34	18.93	17.43	16.97
Paraffinic C_P , %	55.84	56.57	56.28	55.68	55.89	55.76	56.60
Pour point, $^{\circ}\text{C}$	-15	-15	-12	-13	-13	-16	-14
Slack wax properties							
Refractive index n_D^{70}	1.4720	1.4811	1.4732	1.4743	1.4759	1.4738	1.4749
Solidification point, $^{\circ}\text{C}$	53.0	54.0	52.6	54.7	54.1	52.6	52.1
Oil content, % (m/m)	38.6	31.8	28.5	41.6	36.2	48.3	51.3

solidification point increased significantly, which indicates the preservation of the selectivity of the TDAE raffinate dewaxing process.

A graphical illustration of the effect of dewaxing process on the change of the structural composition and pour point of deparaffinates is presented in Figures 2 and 3.

3.2 Dewaxing the TDAE plasticiser with the MIBK–MEK solvent

Table 5 presents technology parameters, mass balance and properties of the obtained deparaffinates and slack waxes, for five MIBK–MEK dewaxing processes of a TDAE

Figure 4: Effect of the dewaxing process with the MBIK–MEK solvent on the change of the structural composition of deparaffinates – TDAE II raw material.

Figure 5: Effect of the dewaxing process with the MBIK–MEK solvent on the change of the deparaffinate pour point – TDAE II raw material.

II raw material sample and two dewaxing processes of the TDAE III raw material sample.

The basic process parameters for dewaxing of the TDAE II raw material were as follows: the mass ratio of MIBK–MEK was in the range from 100:0 to 60:40, the crystallisation temperature was -20 or -28°C and the total solvent to fraction ratio was from 3.5:1 to 7:1. In test 46, a crystallisation modifier was used for the process.

In the dewaxing attempts, the deparaffinate yield was large and ranged from 86.0 to 89.0% (m/m) and the slack wax yield was in the range of 7.0–11.0% (m/m).

Compared to the TDAE II raw material, as a result of the dewaxing process in the TDAE deparaffinate, an increase in the carbon content in aromatic structures in deparaffinate was observed for all tests, which ranged from 1.07 to 1.41%; the content of carbon atoms in naphthenic structures increased max. to 0.20%, or decreased to the max. 0.69%, and the content of carbon atoms in paraffin structures decreased from 0.47 to 1.39%.

In all dewaxing attempts, the pour point in the deparaffinate decreased significantly to the range -12 to -15°C , compared to the raw material whose pour point was $+30^{\circ}\text{C}$.

Compared to deparaffinates and raw material in slack waxes, the refractive index markedly decreased and the solidification point increased significantly, which indicates the preservation of the selectivity of the TDAE raffinate dewaxing process.

In two dewaxing attempts of the TDAE III raw material, the deparaffinate yield ranged from 91.0 to 92.0% (m/m), and the slack wax yield was in the range of 5.0–7.0% (m/m).

Compared to TDAE III raw material, as a result of the dewaxing process, in the TDAE deparaffin, an increase in the content of carbon atoms in aromatic structures was observed in the range of 0.59–0.97%. Significantly reduced pour point occurred in the deparaffinates, -14 to -16°C , compared to the raw material – TDAE plasticiser. Generally, the dewaxing process of the TDAE II and TDAE III raw materials similarly affects the qualitative properties of the deparaffinates and slack waxes obtained from both raw materials.

A graphic illustration of the effect of the dewaxing process on the change of the structural composition and pour point of deparaffinates, for the TDAE II charge, is presented in Figures 4 and 5.

Table 6: Technology parameters, mass balance and properties of the obtained deparaffinates and slack waxes, in MEK–MTBE dewaxing processes of a TDAE II and TDAE III raw material samples

Dewaxing no.	PR 12	PR 13	PR 14	PR 15	PR 16	PR 17	PR 18
Raw material, sample no.	TDAE II	TDAE II	TDAE II	TDAE II	TDAE II	TDAE III	TDAE III
Viscosity modifier	—	Viscoplex 9–350	—	—	—	—	—
Technology parameters of dewaxing processes							
MEK–MTBE solvent, weight ratio	60:40	40: 60	70: 30	60: 40	70: 30	60: 40	40: 60
Crystallisation/filtration temperature, $^{\circ}\text{C}$	-28	-28	-20	-20	-30	-28	-20
Total solvent to fraction ratio	5.0: 1	5.0: 1	7.0: 1	5.7: 1	7.0: 1	5.5: 1	4.0: 1
Mass balance of dewaxing processes, averaged results							
Filtration time, s	72	41	67	94	89	112	125
Deparaffinate yield, % (m/m)	91.0	92.0	92.0	93.0	88.0	89.0	87.0
Slack wax yield, % (m/m)	7.0	6.0	5.0	5.0	9.0	8.0	9.0
Losses, % (m/m)	2.0	2.0	3.0	2.0	9.0	3.0	4.0
Properties of deparaffinate							
Kinematic viscosity at 50°C , mm^2/s	295.8	289.7	298.4	293.5	301.5	329.7	332.4
Kinematic viscosity at 100°C , mm^2/s	24.74	24.74	24.68	24.67	25.12	28.04	28.13
Refractive index n_D^{20}	0.9524	1.5332	1.5333	1.5330	1.5336	0.9527	1.5192
Density at 20°C , g/cm^3	0.9524	0.9528	0.9562	0.9524	0.9565	0.9527	0.9529
Sulphur content, % (m/m)	2.98	2.94	3.02	2.94	3.21	3.30	3.31
PAC content (DMSO extr.), % (m/m)	2.1	2.2	2.2	2.1	2.3	2.8	2.8
Content of carbon atoms in structures							
Aromatic, C_A , %	24.67	24.58	24.86	24.87	25.23	26.28	26.34
Naphthenic, C_N , %	18.49	18.34	18.45	17.94	18.74	18.43	18.25
Paraffinic C_P , %	56.84	57.08	56.69	57.19	56.03	55.29	55.41
Pour point, $^{\circ}\text{C}$	-18	-15	-13	-16	-17	-14	-12
Slack wax properties							
Refractive index n_D^{70}	1.4747	1.4745	1.4712	1.4763	1.4812	1.4835	1.4852
Solidification point, $^{\circ}\text{C}$	54.0	53.6	55.1	55.0	52.7	52.1	51.3
Oil content, % (m/m)	34.7	39.4	36.5	31.8	42.3	61.3	60.5

3.3 Dewaxing the TDAE plasticiser with the MEK–MTBE solvent

Table 6 presents technology parameters, mass balance and properties of the obtained deparaffinates and slack waxes, for five MEK–MTBE dewaxing processes of a TDAE II raw material sample and two dewaxing processes of the sample of raw material TDAE III.

The basic process parameters were as follows: the mass ratio of MEK–MTBE was in the range from 70:30 to 40:60, the crystallisation temperature was -20 or

-30°C and the total solvent to fraction ratio was from 5.0:1 to 7.0:1. In test 54, a crystallisation modifier was used for the process.

In the dewaxing attempts, the deparaffinate yield was large and ranged from 88.0 to 93.0% (m/m) and the slack wax yield was in the range of 5.0–9.0% (m/m).

Compared to the TDAE II raw material, as a result of the dewaxing process in the TDAE deparaffinate, an increase in the carbon content in aromatic structures in deparaffinate was observed for all tests, which ranged from 0.72 to 1.37%; the content of carbon atoms in

Figure 6: Effect of the dewaxing process with the MBIK–MEK solvent on the change of the structural composition of deparaffinates – TDAE II raw material.

Figure 7: Effect of the dewaxing process with the MEK–MTBE solvent on the change of the deparaffinate pour point – TDAE II raw material.

Table 7: Amount of substance and latex parameters during coagulation

Rubber sample	TDAE III/PR19/1	TDAE III/PR19/2
Dry mass of the KER 2712 base latex (%)	25	25
ML of the KER 2712 base latex (MU)	130	130
Dusantox 6PPD stabiliser weight (g)	12	12
TDAE oil weight (g)	344	344

Table 8: Results of physiochemical analysis of the oiled rubber KER 1723 based on TDAEIII/PR19

Rubber sample	Requirements for the KER 1723 oiled rubber	TDAE III/PR19/1	TDAE III/PR19/2
Rolled ML viscosity (MU)	45–55	48.9	50.1
Rolled ML	—	–13.5	–12.8
Acids (%)	4.0–6.0	5.09	5.12
Soaps (%)	max. 0.4	0.13	0.17
Volatile matter content (%)	max. 0.8	0.15	0.19
Ash (%)	max. 0.4	0.36	0.24
TDAE oil content (%)	25–29	28.0	27.9
Bonded styrene (%)	22–25	23.3	23.4

naphthenic structures decreased to min. 0.40% to max. 1.2%; and the content of carbon atoms in paraffin structures increased to 0.09% or decreased to the max. 0.96%.

In all dewaxing attempts, the pour point in the deparaffinate decreased significantly to the range –13 to –18°C, compared to the raw material whose pour point was +30°C.

Compared to deparaffinates and raw material in slack waxes, the refractive index markedly decreased and the solidification point increased significantly, which indicates the preservation of the selectivity of the TDAE raffinate dewaxing process.

In two dewaxing attempts of the TDAE III raw material, the deparaffinate yield ranged from 87.0 to 89.0% (m/m), and the slack wax yield was in the range of 8.0–9.0% (m/m).

Compared to TDAE III raw material, as a result of the dewaxing process, in the TDAE deparaffin, an increase in the content of carbon atoms in aromatic structures was observed in the range 0.44–0.50%. Significantly reduced pour point occurred in the deparaffinates, –12 to –14 °C, compared to the raw material – TDAE plasticiser. Similarly, as for the MEK–MIBK solvent dewaxing process, the MEK–MTBE dewaxing of TDAE II and TDAE III raw materials affects, with the same trend, the qualitative properties of the obtained deparaffinates and slack waxes from both raw materials.

A graphical illustration of the effect of the dewaxing process on the change of the structural composition and pour point of deparaffinates is presented in Figures 6 and 7.

3.4 Application tests on a laboratory scale of the TDAE plasticiser for oiled rubber

In the framework of the study, application tests for modified TDAE plasticiser applied were performed to produce oiled rubber KER 1723 and standard rubber compounds.

Raw material – oiled rubbers for the application test were the modified TDAE plasticiser obtained in the process of selective refining with furfural and the subsequent dewaxing process with the MEK–TOL solvent, which was identified by code TDAE III/PR 19.

To compare the evaluation of the physiochemical properties of oiled rubber containing modified TDAE plasticiser, with requirements for KER 1723 oiled rubber, two coagulations were carried out with the oil in question

Table 9: Composition of rubber compound based on the oiled rubber KER 1723 contained in TDAE III/PR19

No.	Component	Unit, phr	Mass, g
1.	KER 1723 oiled rubber	100.00	600.0
2.	Zinc white	3.00	18.0
3.	Stearin	1.00	6.0
4.	Sulphur	1.75	10.5
5.	Soot IRB	50.00	300.0
6.	TBBS accelerator – (N-tert-butyl-2-benzothiazolylsulfonamide)	1.00	6.0
Total		156.70	940.5

Table 10: Physicomechanical properties of the rubber compound based on the KER 1723/TDAE III/PR19/1 and the KER 1723/TDAE III/PR19/2

Rubber compound sample	Rubber compound requirements	KER 1723/TDAE III/PR19/1	KER 1723/TDAE III/PR19/2
Mixture ML viscosity (MU)	—	53.7	52.8
Maximum vulcanisation curve (dNm)	13.5–16.5	15.19	14.94
Minimum vulcanisation curve (dNm)	1.8–2.7	1.94	1.92
TS1 (min)	2.0–5.0	3.72	3.57
T10 (min)	—	4.14	3.96
T25 (min)	—	5.33	5.12
T50 (min)	5.0–9.0	6.77	6.63
T90 (min)	12.0–17.0	12.94	13.36
Tensile strength (MPa)	Minimum 20	20.7	21.6
Elongation at rupture (%)	Minimum 320	409	427
Stress at 300% elongation (MPa)	13–17	14.5	14.4
Hardness (°ShA)	60–66	63.5	63.7
Flexibility, Schob method (%)	Minimum 28	40.3	41.6

marked with symbols: TDAE III/PR19/1 and TDAE III/PR19/2. The obtained oiled rubber sample KER 1723 was subjected to laboratory tests for the evaluation of physicochemical and physicomechanical properties. The results of the tests are listed in Tables 7 and 8.

Laboratory-scale application tests proved that physiochemical properties of the oiled rubber KER 1723 contained the modified plasticiser TDAE III/PR19 to meet the quality requirements of SYNTOS SA in the scope of physiochemical parameters required for oiled rubber.

Further application tests involve the preparation of a standard rubber compound from the KER 1723/TDAE III/PR19 oiled rubber according to ASTM D 3185, Recipe 1 A. The composition of the rubber mixture is presented in Table 9.

Rubber compounds based on the KER 1723 oiled rubber were subjected to laboratory tests to evaluate the physiochemical properties and performance characteristics, which are presented in Table 10.

The analysis of the results of rubber compound application tests of rubber made of the KER 1723 oiled rubber contained the modified TDAE III/PR19 plasticiser showed that physicomechanical properties of the vulcanisates meet the requirements specified by SYNTOS SA for reference rubber mixtures.

4 Conclusion

Studies of the solvent dewaxing process with various mixtures, MEK–TOL, MIBK–MEK and MEK–MTBE were carried out for three different TDAE plasticisers.

It was demonstrated that solvent dewaxing of the TDAE plasticiser with positive pour points, meeting the

requirements of the Regulation 1907/2006 EU, maintains good process selectivity and allows for a significant reduction of the plasticiser pour point, thus improving the rheological and low-temperature properties.

In all dewaxing attempts, the pour point in the deparaffinate decreased significantly to the range –12 to –22°C, compared to the positive pour points of the raw materials.

For the solvents studied, the effect of lowering the pour point of the TDAE plasticiser in the solvent dewaxing process was obtained, while maintaining quality parameters meeting the requirements of REACH, which can be considered as obtaining a modified TDAE plasticiser with a minus pour point, which should have a positive effect on improving the rubber performance in low product temperatures, particularly the car tyres.

The results achieved in the solvent dewaxing process with the mixture of MEK–TOL, MIBK–MEK and MEK–MTBE and the TDAE plasticiser used for the raw material cause slight shifts in the structural composition of deparaffinate, compared to the raw material and do not significantly improve the desired aromatic structure of TDAE raffinates. However, in the assessment of the structural composition of hydrocarbons presented, it should be noted that the structural composition according to ASTM D 2410 [34] is calculated indirectly and may not fully reflect the actual structural change of hydrocarbons after the dewaxing process.

In the attempts of plasticiser dewaxing studied, no favourable change in the structural composition of hydrocarbons was achieved, in particular when it comes to increasing the content of carbon atoms in aromatic structures, compared to the dewaxing charge. Similarly, the content of carbon atoms in naphthenic structures, for some dewaxing tests, increases slightly, while for other tests it decreases, compared to the raw material. Also, the content

of carbon atoms in paraffin structures does not decrease much or increases in comparison to the raw material, while the content of paraffins would be desired to significantly decrease, thus improving mainly the content of the aromatic compounds.

Studies on the use of modified plasticisers to produce oiled rubber and vulcanisate meet the quality requirements for those products with regard to the physical and mechanical properties specified by SYNTOS SA.

The study conducted allowed for the preparation of four patent applications with the Patent Office of the Republic of Poland.

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