Research Article

Stefan Ptak*, Wojciech Krasodomski, Janusz Jakóbic, Artur Antosz

Modified TDAE petroleum plasticiser

https://doi.org/10.1515/chem-2021-0081
received May 25, 2021; accepted August 4, 2021

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 deparaflinate. 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–MBK 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 deparaflinate 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].
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 oilied 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 ≤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

| Properties | MES | TDAE | Heavy naphthenic (HNAP) |
|------------|-----|------|-------------------------|
| Content of carbon atoms in structures: Ca, % | 11–17 | 25–30 | 11–17 |
| Density at 15°C, g/cm³ | 0.895–0.925 | 0.930–0.960 | 0.920–0.950 |
| Viscosity at 40°C, mm²/s | 150–230 | 370–430 | 350–720 |
| Viscosity at 100°C, mm²/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, Tg, °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 |

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

| Properties | Raw material | Extract I | Extract II | Extract III | Test methods |
|------------|--------------|-----------|------------|-------------|--------------|
| Density at 20°C, g/cm³ | | 0.9749 | 0.9893 | 0.9916 | PN-EN ISO 12185 |
| Kinematic viscosity at 50°C, mm²/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 | ASTM D 2140 |
| 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,k)fluoranthene | | 24.2 | 14.7 | 14.3 | |
| Dibenz(a,h)anthracene | | 3.5 | 2.3 | 1.8 | |
| Total PAHs | | 97.7 | 79.9 | 68.8 | |
Table 4: Technology parameters, mass balance and properties of the obtained deparaaffinates 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 |
| Deparaaffinate 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 deparaaffinate | | | | | |
| Kinematic viscosity at 50°C, mm²/s | 152.9 | 138.4 | 156.3 | 153.4 | 289.3 |
| Kinematic viscosity at 100°C, mm²/s | 16.49 | 15.68 | 16.58 | 16.78 | 24.17 |
| Refractive index n²⁰ | 1.5253 | 1.5245 | 1.5256 | 1.5258 | 1.5330 |
| Density at 20°C, g/cm³ | 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, C₅₆, % | 21.28 | 20.99 | 21.51 | 21.73 | 24.09 |
| Naphthenic, C₉₄, % | 20.61 | 19.87 | 19.98 | 19.42 | 18.41 |
| Paraffinic Cₛₚ, % | 58.11 | 59.14 | 58.51 | 58.85 | 57.50 |
| Pour point, °C | −15 | −15 | −22 | −14 | −15 |
| Slack wax properties | | | | | |
| Refractive index n²⁰ | 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 |

Table 3: Physiochemical properties of TDAE plasticisers

| Properties | Plasticiser | Test methods |
|------------|-------------|--------------|
| Density at 20°C, g/cm³ | TDAE I | TDAE II | TDAE III | PN-EN ISO 12185 |
| Kinematic viscosity at 100°C, mm²/s | 15.33 | 22.29 | 24.47 | PN-EN ISO 3104 |
| Flash point, (°C) | 276 | 271 | 271 | PN-EN ISO 2592 |
| Refractive index n²⁰ | 1.5223 | 1.5302 | 1.5349 | PN-C-04952:81 |
| Sulphur content, % (m/m) | 2.5366 | 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 | | | | |
| Aromatic, C₅₆, % | 20.3 | 23.86 | 25.84 | ASTM D 2160 |
| Naphthenic, C₉₄, % | 24.2 | 19.14 | 16.49 | | |
| Paraffinic Cₛₚ, % | 55.5 | 56.99 | 57.67 | | |
| PAH content, mg/kg | | | | |
| 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,i)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 | | |
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 deparaftinates 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 out.

![Figure 2: Effects of the dewaxing process with the MEK–TOL solvent on the change of the structural composition of deparaftinates – TDAE I raw material.](image)

![Figure 3: Effect of the dewaxing process with the MEK–TOL solvent on the change of the deparaftinate pour point – TDAE I raw material.](image)
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°C.

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

| Table 4: 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 |
|---|---|---|---|---|---|---|---|---|
| Raw material, sample no. | PR 05 | PR 06 | PR 07 | PR 08 | PR 09 | PR 10 | PR 11 |
| Viscosity modifier | — | 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, °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, mm²/s | 313.8 | 258.8 | 294.7 | 318.9 | 297.4 | 323.4 | 318.2 |
| Kinematic viscosity at 100°C, mm²/s | 25.24 | 23.09 | 24.63 | 25.67 | 24.93 | 27.83 | 27.48 |
| Refractive index n₂⁰ | 1.5134 | 1.5338 | 1.5338 | 1.5334 | 1.5336 | 1.5387 | 1.5184 |
| Density at 20°C, g/cm³ | 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, Cₐ, % | 25.27 | 24.98 | 24.93 | 24.98 | 25.18 | 26.81 | 26.43 |
| Naphthenic, Cₙ, % | 18.89 | 18.45 | 18.79 | 19.34 | 18.93 | 17.43 | 16.97 |
| Paraffinic Cₚ, % | 55.84 | 56.57 | 56.28 | 55.68 | 55.89 | 55.76 | 56.60 |
| Pour point, °C | −15 | −15 | −12 | −13 | −13 | −16 | −14 |
| Slack wax properties | | | | | | | |
| Refractive index n₂⁰ | 1.4720 | 1.4811 | 1.4732 | 1.4743 | 1.4759 | 1.4738 | 1.4749 |
| Solidification point, °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 II raw material.

**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 deparaftinate 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 deparaftinate, an increase in the carbon content in aromatic structures in deparaftinate 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 deparaftinate decreased significantly to the range −12 to −15°C, compared to the raw material whose pour point was +30°C.

Compared to deparaftinates 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 deparaftinate 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 deparaftinate, 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 deparaftinates, −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 deparaftinates 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 deparaftinates, for the TDAE II charge, is presented in Figures 4 and 5.

Table 6: Technology parameters, mass balance and properties of the obtained deparaftinates 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 | — | — | — | — | — | — | — |
| 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, °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 |
| Dепаftinate 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 deparaftinate | | | | | | | |
| Kinematic viscosity at 50°C, mm²/s | 295.8 | 289.7 | 298.4 | 293.5 | 301.5 | 329.7 | 332.4 |
| Kinematic viscosity at 100°C, mm²/s | 24.74 | 24.74 | 24.68 | 24.67 | 25.12 | 28.04 | 28.13 |
| Refractive index nD²⁰ | 0.9524 | 1.5332 | 1.5333 | 1.5330 | 1.5336 | 0.9527 | 1.5192 |
| Density at 20°C, g/cm³ | 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, Cₐ, % | 24.67 | 24.58 | 24.86 | 24.87 | 25.23 | 26.28 | 26.34 |
| Naphthenic, Cₙ, % | 18.49 | 18.34 | 18.45 | 17.94 | 18.74 | 18.43 | 18.25 |
| Paraffinic, Cₚ, % | 56.84 | 57.08 | 56.69 | 57.19 | 56.03 | 55.29 | 55.41 |
| Pour point, °C | −18 | −15 | −13 | −16 | −17 | −14 | −12 |
| Slack wax properties | | | | | | | |
| Refractive index nD²⁰ | 1.4747 | 1.4745 | 1.4712 | 1.4763 | 1.4812 | 1.4835 | 1.4852 |
| Solidification point, °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.
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 deparaffinates 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 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            |

### 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   |
marked with symbols: TDAE III/PR19/1 and TDAE III/PR19/2. The obtained oilied rubber sample KER 1723 was subjected to laboratory tests for the evaluation of physiochemical 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 oilied 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 oilied rubber.

Further application tests involve the preparation of a standard rubber compound from the KER 1723/TDAE III/PR19 oilied 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 oilied 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 oilied 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 depaffinate 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 deparaflinate, 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.

Acknowledgements: The authors would like to thank Synthos S.A. for performing the application tests for the sample of the modified TDAE plasticiser provided. The article was written on the statutory work entitled: Assessment of the TDAE plasticizer on the quality requirements of rubber products – supported by the Oil and Gas Institute – National Research Institute commissioned by the Ministry of Science and Higher Education, archive number: DK-4100-/80/17, order number: 0093/TO/17.

Funding information: This work was supported by the Oil and Gas Institute – National Research Institute (INIG – PIB) statutory work no. DK-4100-/80/17.

Author contributions: S.P. – supervision, conceptualization, formal analysis, investigation, writing – original draft; W.K. – conceptualization, formal analysis, writing – review & editing; J.J. – validation, writing – review & editing; A.A. – data curation, visualization, writing – review & editing.

Conflicts of interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Ethical approval: The conducted research is not related to either human or animal use.

Data availability statement: All data generated or analysed during this study are included in this published article.

References

[1] Rocha TCJ, Soares BG, Coutinho FMB. The most important butadiene based elastomers employed in the automotive industry. Polimeros. 2007;17(4):299–307.

[2] Bastardo-Zambrano L. The global naphthenic market: present and future challenges and opportunities. Kraków: NYNAS; 2011.

[3] Ptak S. Evaluation of the process solvent dewaxed plasticizer TDAE. Nafta-Gaz-Sci Technol Oil Gas Ind. 2017;8:605–15.

[4] Pocklington JE. Safer Alternatives to aromatic process oils. Tire Technology International; 1998. p. 43–7.

[5] Mobil Europe Lubricants Limited, UK. An article “Oils without labels”. Tire Technology International; 1999. p. 10.

[6] Null V. Rubber tests with safer extender oils. Tire Technology International; 1999. p. 21–5.

[7] Regulation (EC) no 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH).

[8] International standard ISO 6743-10:1989 Lubricants, industrial oils and related products (class L) – Classification Part 10: Family Y (Miscellaneous)).

[9] Garbim VJ. Plastificantes para compostos de borracha. Borracha Atual. 2001;23:14–29.

[10] Ezoddin S, Abbassian A, Aman-Alikhani M, Taghvaei S. The influence of non-carcinogenic petroleum-based process oils on tire compounds’ performance. Iran Polym J. 2013;22(9):697–707.

[11] Ptak S. Petroleum plasticizers for rubber industry – dewaxing TDAE plasticizer. Nafta-Gaz-Sci Technol Oil Gas Ind. 2017;9:675–84.

[12] Li Y, Yin J, Pan H. Petroleum plasticiser for tyre manufacturers. Pet Process Petrochem. 2011;42(26):126–31.

[13] Dasgupta S, Agraval SL, Bandyopadhyay S, Chakraborty S, Mukhopadhyay R, Mallani RK, et al. Characterization of eco-friendly processing aids for rubber compound. Polym Test. 2007 June;26(4):489–500.

[14] Chiossos WC. SBR rubber plasticisers. Borracha Atual. 2007;71(5):34–39.

[15] Zamboni GE. Extrato aromatico. Lubes em Foco; 2007;2:25–7.

[16] Bowman J, da Via M, Pattnelli ME, Tortoreto P. The influence of non-Toxic extender oil on SBR performances. Kautsch Gummi Kunstst. 2004;57(1–2):31–6.

[17] Patent application EP 3 031 621 A1. Pneumatic tire. The conducted research is not related to either human or animal use. BP Oiltech GMBH; pub. date 21.03.1991.

[18] Patent EP 839891. Process for obtaining aromatic oils having a polycyclic aromatics content of less than 3% which are useful as process oils. Repsol Petroleo SA; pub. date 06.05.1998.

[19] Patent DE 2343238. Verfahren zur behandlung von mineral schmierol-ausgangs materialien. British Petroleum CO; pub. date 14.03.1974.

[20] Patent EP 1006673. Removal of polycyclic aromatic compounds from extracts. Shell Int Research; pub. date 13.06.2001.

[21] Patent EP 1260569. Process for making non-carcinogenic, high aromatic process oil. Shell Int Research; pub. date 27.11.2002.

[22] Patent PL 207051. The manner of production of oil plasticizer for caoutchouk and rubber Oil and Gas Institute. Group Lotos SA; pub. date 29.10.2010.

[23] Patent PL 224956. Method for preparing an oil plasticizer for raw rubber and rubber oil and gas Institute. Group Lotos SA; pub. date 28.02.2017.
[26] Patent PL 207052. Method for the manufacture of TDAE plasticizer for natural rubber and rubber. Oil and Gas Institute. Group LOTOS S.A; pub. date 29.10.2010.

[27] Patent PL 207056. The manner of production of TDAE plasticizer. Oil and Gas Institute; pub. date 29.10.2010.

[28] Patent PL 208531. Plasticizer and method for producing a plasticizer. ZAKRYTOE AKTSIONERNOE OBSCHESTVO TORGOVY DOM “ORGKHIM”; pub. date 31.05.2011.

[29] Patent application WO2011098096 A1. Method for producing process oils having a low content of polycyclic aromatics and use thereof. H & R International GMBH; pub. date 10.02.2010.

[30] Patent DE 2827494. Verfahren zur entparaffinierung von paraffinhaltigem schmieröl ausgangs material, Texaco Development Corp; z dnia 25.01.1979.

[31] Patent US 3972779. Means for controlling dewaxing apparatus. Texaco INC; pub. date 03.08.1976.

[32] Patent US 4146461. Dilution chilling dewaxing by modification of tower temperature profile. Exxon Research Engineering Co; pub. date 27.03.1979.

[33] Patent US 4444648. Solvent dewaxing with methyl tertiary butyl ether. Exxon.

[34] Standard ASTM D 2410:2015. Standard test method for carbon-type composition of insulating oils of petroleum origin.