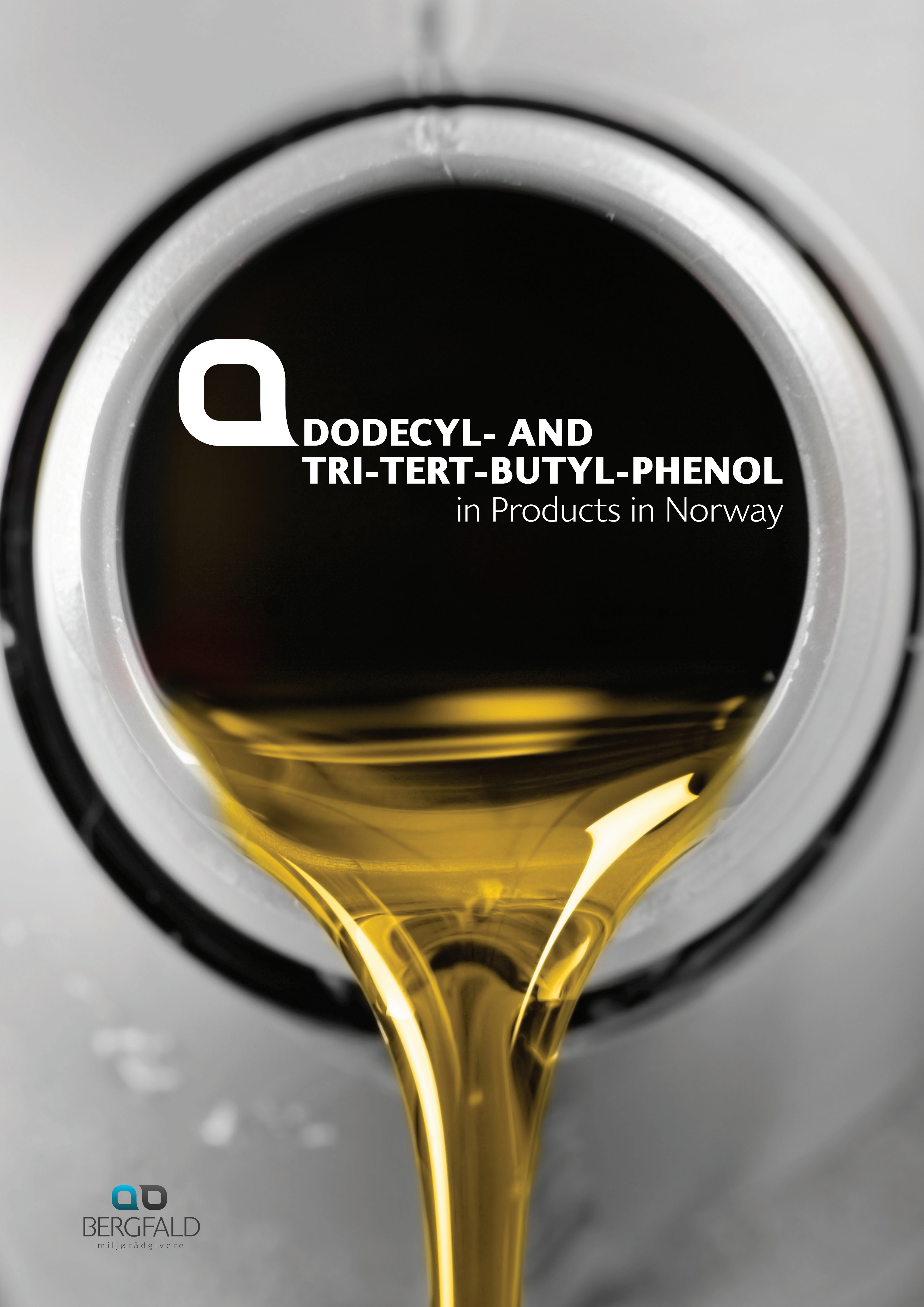


DODECYL- AND TRI-TERT-BUTYL-PHENOL

in Products in Norway

BERGFALD
miljørådgivere

DODECYL- AND TRI-TERT-BUTYL-PHENOL
in Products in Norway

TA-NR 2744/2010

Project carried out for the Climate and Pollution Agency (Klif)
December 2010

Nicole Lambert
Christian Rostock
Anders Bonden

BERGFALD
miljørådgivere

TA-NR 2744/2010: DODECYL- AND TRI-TERT-BUTYL-PHENOL IN PRODUCTS IN NORWAY
Published: **OSLO/DECEMBER 2010. BERGFALD MILJØRÅDGIVERE, KONGENS GATE 3 0153 OSLO.**
PH.: +47 23 00 05 90. E-MAIL: INFO@BERGFALD.NO. WWW.BERGFALD.NO
Authors: **NICOLE LAMBERT, CHRISTIAN ROSTOCK, ANDERS BONDEN**
Layout: **GAUTE HAUGLID-FORMO**
Project carried out for: **THE CLIMATE AND POLLUTION AGENCY (KLIF)**

BERGFALD
miljørådgivere

SUMMARY

The following study has been carried out in the context of the national objective to reduce the environmental emission of hazardous chemicals, listed on the priority list.

The objective of this report was to identify the applications of Dodecyl-phenols (DDPs) and 2,4,6 tris-tert-butyl-phenol (TTBP) in Norway, estimating the quantities potentially imported to Norway via products and defining the potential environmental emission patterns related to the life cycle of these products.

The use of previous studies on the topic and broad internet research constituted the base of the methodology used. In addition, in order to establish more specifically the pattern of use of these chemicals, Norwegian and international manufacturers and manufacturer associations were contacted.

Data found shows that in Norway the main use of TTB-phenol resides in its potential use as a fuel additive. It will be used only in hydrotreated fuel, which is not a process used in Norwegian refineries. Consequently TTBP will only be found in imported fuel, and will represent a minim constituent of the fuel (ca. 0,027%). With normal use, TTBP will burn and environmental emission will not be of any significance. DDPs are expected to be imported mainly in crankcase lubricants, for automotive and marine purposes. Indeed DDPs appear to be a common additive used in the manufacturing of crankcase lubricants. Not all lubricant manufacturers indicate the presence of the chemical on their MSDS, though they are used and not all are expected to register the chemical in the Product Register. DDPs will represent a minor component of the lubricant. The disposal of used oil has been identified as the main source of environmental emission of DDPs. This has been further supported by screening data that detected DDPs in significant amounts in sewage treatment plants.

DDPs may also enter the composition of phenolic resins, in particular Novalec resins. The application range of these resins is broad and DDPs do not appear to be commonly used. Furthermore DDPs are expected to be present in minim quantities in the final products (e.g. tyre rubber, inks). The environmental emission of the DDPs via material composed of phenolic resins is expected to be low and the environmental availability of DDPs in the material is debatable.

There is little environmental concern as regards to the presence of TTBP in products in Norway. However, as regards to DDPs, their presence appears to be common in crankcase lubricants and the emission via uncontrolled disposal of engine oil could be of significant environmental concern.

SAMMENDRAG

Denne studien har blitt gjennomført i forbindelse med det nasjonale målet å redusere utslippene av farlige kjemikalier til naturen, stoffer oppført på prioritets-listen.

Målsetningen med rapporten har vært å identifisere bruksområder for dodekylfenoler og 2,4,6 tri-tert-butylfenol i Norge og bestemme mengdene som potensielt blir importert via produkter. Potensiell miljøeksponering i forbindelse med livssyklusen til disse produktene har også blitt bestemt.

Bruk av tidligere rapporter og internettsøk er grunn-fjellet i metoden som er brukt. For å fremskaffe mer spesifikke bruksområder for kjemikaliene har norske og internasjonale produsenter og produsentorganisasjoner blitt kontaktet.

Funnene viser at det viktigste bruksområdet for TTB-fenol er at den kan brukes som additiv til drivstoff og smøremidler. Den blir kun brukt i hydroprosessering som ikke er en prosess som brukes i norske raffin-erier. Bruken av TTB vil derfor kunne være i importert drivstoff og vil være en liten bestanddel av denne (ca. 0,0027%). Ved normal bruk vil fenolen forbrenne og utslippet til naturen være neglisjerbart.

Dodekylfenol forventes å hovedsakelig importeres via motoroljer til biler, lastebiler, busser og marine fartøyer. Fenolen er et vanlig additiv i motoroljer. Ikke alle produsenter viser til at kjemikaliet er bruk i deres sikkerhetsdatablader og det er dermed heller ikke forventet at alle registrerer bruken i produktregis-teret. DD-fenol er en mindre komponent i motoroljer. Ulovlig behandlingen av brukt olje har blitt identifisert som hovedkilden til utslipp av dodekylfenol til naturen. Dette blir videre bekreftet av undersøkelser som finner kjemikaliet i vesentlige mengder i renseanlegg for avløpsvann.

Dodekylfenol vil også være en del av fenolharpikser, spesielt novolac harpiks. Bruksområdet for disse harpiksene er bredt og dodekylfenol ser ikke ut til å være en vanlig bestanddel. Videre vil dodekylfenol være en liten bestanddel i det ferdige produktet (f.eks. gummi til bildekk og blekk). Utslippet til naturen av dodekylfenol via materialer bestående av fenolhar-pikser forventes å være lavt og tilgjengeligheten av dodekylfenol til naturen fra materialet er diskutabelt.

Det er lite miljømessig bekymring med tanke på tri-tert-butylfenol i produkter i Norge. Derimot ser det ut til at dodekylfenol er vanlig i motoroljer og at utslipp fra ulovlig disponering av motorolje kan være et vesentlig problem for miljøet.

CONTENTS

1. INTRODUCTION

Norway has a national objective to reduce the emission of hazardous chemicals in the environment. In order to do so, in a first stage such substances need to be identified as regards to their toxicity, persistence and bioaccumulation potential. The second stage requires defining their actual presence in the Norwegian environment, by documenting their use and their potential emission. The information gathered in these two stages will allow the authorities to assess the need for further measures.

The toxicity, persistence and bioaccumulation potential of Dodecyl phenols (DDPs) and 2,4,6, tri-tert-butyl-phenol (TTBP) have been assessed and designated as hazardous and both components have been listed on the chemical priority list "Nye stoffer hvis utslipp skal reduseres vesentlig innen 2020"[1], consequently Norway is committed to significantly reducing the emission of these components by 2020.

The objective of this report is to technically support the emission reduction aimed for by Norway, by documenting where and how the reductions could potentially be carried out.

LIST OF ABBREVIATIONS

ATC	Additives Technical Comitee
CAS	Chemical Abstracts Service
CEPAD	European Council for Alkylphenols and Derivatives
CMR	Carcinogenic, Mutagenic or Toxic to Reproduction
DDP	Dodecyl phenol
DEFRA	The Department for Environment, Food and Rural Affairs (UK)
ERMA	European Resins Manufacturers Association
ESIS	European Chemical Substances Information System
ETRA	The European Tyre Recycling Association
HSDB	Hazardous Substances Data Bank
Klif	Climate and pollution agency
MSDS	Material Safety Data Sheet
PBT	Persistent Bioaccumulative Toxic
SSB	Statistics Norway
STN	Scientific & Technical Information Network
STP	Sewage Treatment Plant
TTBP	2,4,6-tri-tert-butyl phenol
T	Toxic
TT	Toxic threshold

2. METHODOLOGY

2.1. OBJECTIVE

This project shall strive to document in what industrial processes and products DDP isomers and TTBP are used, and in what quantities, thereby defining the expected emission routes and estimating the annual quantities used/imported in Norway. This project shall also look into methodologies available to estimate the environmental emission of the compounds.

2.2. DDP AND TTBP IN PRODUCTS IN NORWAY

First internet and in particular the STN database, operated jointly by Chemicals Abstracts Service and FIZ Karlsruhe, was used in order to make an inventory of all registered applications for DDP and TTBP. STN is the most comprehensive source for product information in the world. Research was carried out using both the CAS registry numbers and different substance name synonyms.

In a second stage, a telephone/email survey was carried out among major international and national industrial actors in the application fields of DDP and TTBP. The responses gave a more clear idea as regards to the current uses of the chemicals internationally and nationally. According to information provided, in particular by national actors, products potentially containing DDP or TTBP were identified and an estimate of the tonnage of DDP and TTBP potentially imported in Norway was made. There is no domestic production of these substances in Norway.

2.3. EMISSIONS OF DDP AND TTBP

International experience relative to the emission of DDP and TTBP is presented in this report. The methodologies used in these studies to estimate the emissions are discussed as regards to the possibility to transpose the methodology to Norwegian conditions.

The methodologies used in previous studies have been adjusted to Norwegian conditions and a methodology is proposed to estimate the emissions of DDP and TTBP in Norway.

3. GENERAL SUBSTANCE INFORMATION

3.1. IDENTIFICATION OF THE COMPONENTS

DDP and TTBP are isomers and have the same chemical formula $C_{18}H_{30}O$.

DDP is distinguished from TTBP by its long, sometimes branched, alkyl (C_{12}) chain, TTBP is recognised by its 3 tertiary branched butyl groups symmetrically placed around the phenol ring.

DDP exists as several isomers, resulting from different substituent locations of the alkyl (C_{12}) chain on the phenol ring and from the degrees of branching of the chain.

Table 1 presents the isomers that shall be considered throughout this document.

As regards to DDPs, 4-dodecyl-phenols are the isomers of greatest interest. A technical grade of DDP contains approximately 85 % 4-DDP, 10 % 2-DDP and 5 % 2,4-di-DDP, and a high purity grade contains approximately 95 % 4-DDP, 2 % 2-DDP and only traces of 2,4-di-DDP.[10] Analytical grades of these chemicals are also available, but are not of interest to this study. The following DDP isomers are the most commonly named in material safety data sheets (MSDS):

- CAS nr.104-43-8
- CAS nr.210555-94-5
- CAS nr. 74499-35-7
- CAS nr. 11067-80-4
- CAS nr. 121158-58-5

The other DDP isomers referred to in Table 1 are by-products (or impurities that have no specific industrial function).

DDPs and TTBP manufacturers were contacted internationally, the majority indicated a net decrease in their production within the last five years, and some have even ceased to produce these chemicals. This should correlate directly with a reduction in use of DDPs and TTBP.

3.2. PBT OVERVIEW

This section shall review briefly the persistence, bioaccumulation and toxicity of DDP and TTBP.

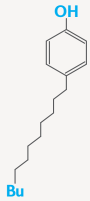
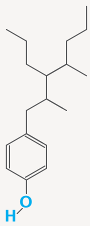
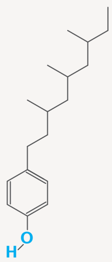
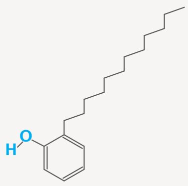
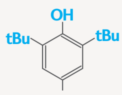
The Nordic screening group reviewed in 2008 the phenolic substances in the Nordic environment.[11] In this report DDP were assessed and the following conclusions were made as regards to the PBT properties of the components:

- DDPs are expected to partition predominantly into sediment and are expected to be persistent in sediment.
- DDPs are highly bioaccumulative
- DDPs are very toxic to fish.

Environment Canada carried out an assessment of TTBP in 2008[12] and the conclusions were the following:

- TTBP does not degrade quickly in the environment and is expected to be persistent in water, soil and sediments.
- Empirical and modelled data indicate that TTBP has the potential to accumulate in organisms and may biomagnifiy through trophic levels in food chains.
- Acute aquatic toxicity values suggest that TTBP is highly hazardous to aquatic organisms.

TABLE 1: GENERAL IDENTIFICATION OF DDP AND TTBP

CAS NR	CHEMICAL FORMULA	CHEMICAL STRUCTURE	IUPAC NAME	SYNONYMS	REF
104-43-8	C18H30O		4-dodecylphenol	para-dodecylphenol Laurylphenol	Esis[2]
11067-80-4	C18H30O		isododecylphenol		Esis[3]
27193-86-8	C18H30O		dodecylphenol		Esis[4]
57427-55-1	C18H30O		4-(2,4-dimethyl-3-propyl-heptyl)phenol	Phenol, tetrapropylene	Pubchem[5]
74499-35-7	C18H30O		tetrapropenyl phenol (TPP)	Tetrapropenyl phenol (TPP)	DEFRA UK[6]
121158-58-5	C18H30O		Phenol, dodecyl-, branched mixed isomers	Lauryl phenol	IRIS[7]
210555-94-5	C18H30O		phenol, 4-dodecyl-, branched		Pubchem[8]
5284-29-7	C18H30O		2-dodecylphenol	orto-dodecylphenol	
732-26-3	C18H30O		2,4,6-tris(1,1-dimethylethyl) phenol	2,4,6-tri-tert-butylphenol 2,4,6-Tri-tert-butylhydroxybenzene; Alkofen B; P 23; TM02; Voidox; 2,4,6-tris(1,1-dimethylethyl)-phenol; tributylphenol,96%; Antioxidant 246; 2,4,6-tri-tertiary butyl phenol (TTBP)	HSDB[9]

4. APPLICATIONS OF DDP AND TTBP

4.1. APPLICATIONS FOR DDP
Applications found for DDP are listed in Table 2. The STN database was the main source used to compose this list and it is important to mention that many of these applications are extracted from patents. In this manner, some of these applications should be considered as potential applications rather than common applications for these components.

(The DDP isomer is specified by its CAS number when this was specifically indicated in the data gathered.)

In addition, DDPs were suspected to be potentially used in cleaning products in Norway, as it was registered within the category of "cleaning agents" in the Product Register. The patent of one cleaning agent suggested the possible use of DDP within the composition of the product; however DDP was one out of many other alternatives.

TABLE 2: APPLICATIONS FOR DDP

CAS NR.	APPLICATION FIELD	SPECIFIC APPLICATIONS
104-43-8	An additive in fuel, oil, gasoline or lubricants.	In the UK 99% of the consumption volume is used in the production of oil and lubricant additives, primarily calcium alkyl phenate sulphides.[13]
74499-35-7	An additive in fuel, oil, gasoline or lubricants.	74499-35-7 can be used as an additive to a refined hydrocarbon based anti-freeze.[14] 74499-35-7 can be used as an additive to a new generation of premium hydraulic oil designed for outdoor use, even at very low temperatures.[15]
121158-58-5	An additive in fuel, oil, gasoline or lubricants.	121158-58-5 is used as an additive to lubricant oil.[16, 17, 18] 121158-58-5 is used as an additive to engine oil[19] including oil for marine engines[20]
104-43-8	Chemical intermediate/catalyst	4-dodecylphenol is converted to a calcium phenolate [50910-68-4] and used as a detergent in lubricating oils.[21] The reaction product of 4-dodecylphenol with ethylene oxide and propylene oxide is used as a corrosion inhibitor in oil.[22] 104-43-8 4-dodecylphenol is used in the production of a zinc dithiophosphate ester [54261-67-5], which is used as an antioxidant and antiwear additive for high temperature applications.[23] High purity 4-dodecylphenol is used to produce specialty surfactants by its reaction with ethylene oxide.[24] 4-dodecylphenol is also used as an epoxy curing catalyst where the addition of 4-dodecylphenol accelerates curing of the epoxy resin to a hard, nontacky solid[25]
	Additive to rubber and plastics	The adhesiveness of resin containing synthetic rubber gum mixtures, useful in tyre manufacturing, was improved without affecting the vulcanization properties while assuring sufficient thermal aging resistance of vulcanizates, by using resins prepd. from (di)alkyl phenols (including DDP) and hexamethylenetetramine or amine- or NH3-HCHO mixes. as resin additives.[26] The maximum concentration of free para-C12-alkylphenols in the resins used to make tyres is assumed to be 3%.[27] Alkyl phenolic resin for use in any part of rubber tyre comprises adding alkylphenol.[28] Antioxidant-fungicides used in the elastomers comprise dodecylphenol among other components.[29]
All	Other	Seed dressing emulsions can be stabilized by phenols and saturated and unsaturated alcohols, including DDP[30]
104-43-8	Phenolic resins	4-dodecylphenol is also used to produce phenolic resins which are used in adhesive applications and printing inks[31]
All p-DD	Phenolic resins	Is used to make phenolic resins. The phenol/formaldehyde resins may be made with para-C12-alkylphenols alone or, more commonly, in admixture with other phenols depending on the properties desired for the final resin. The resins may contain up to 3% of unreacted para-C12-alkylphenols[32]
11067-80-4	Other	Dyeing of cellulosic materials (cotton), includes ethylene oxide-isododecylphenol reaction product in one of the 4 stages of dyeing. It is one of the components in the fixation mix.[33]
121158-58-5	other	121158-58-5 (mixed dodecyl phenol isomers) is used as an additive to a benzyl alcohol based two- component solvent-free seamless coating for flooring.[34]

TABLE 3: PROPERTIES OF DDP[37]

APPLICATION	FUNCTION
Lube oil additive	4-dodecylphenol is converted to a calcium phenolate [50910-68-4] and used as a detergent in lubricating oils. The phenolate combines with combustion debris to prevent the accumulation of the debris on engine parts and neutralizes the strong acids formed during combustion and oxidation.
Lube oil additive	The reaction product of 4-dodecylphenol with ethylene oxide and propylene oxide is used as a corrosion inhibitor in oil. It coats the inner surfaces of an engine to prevent the corrosion of moving parts.
Lube oil additive	4-dodecylphenol is used in the production of a zinc dithiophosphate ester [54261-67-5], which is used as an antioxidant and antiwear additive for high temperature applications.
Production of surfactants	High purity 4-dodecylphenol is used to produce specialty surfactants by its reaction with ethylene oxide. The slight colour of high purity 4-dodecylphenol is important in this application from a standpoint of aesthetics.
Produce phenolic resins	4-dodecylphenol is also used to produce phenolic resins which are used in adhesive applications and printing inks.
Epoxy resins	4-dodecylphenol is also used as an epoxy curing catalyst where the addition of 4-dodecylphenol accelerates curing of the epoxy resin.

Research was also carried out in order to identify any potential uses in cosmetics, or pharmaceuticals. Research carried out on internet showed no potential use in these sectors.

Products DDP will be found in are:

- Additive to crankcase lubricants (automotive and shipping)
- Constituent in phenolic resins (e.g. rubber, ink)
- Epoxy resins (e.g. paints, adhesives)

Internationally the major application (over 95 %) of DDP is recognized to be in the production of oil and lubricant additives.[35, 36] There is no indication that the pattern should be different for Norway.

4.2. FUNCTIONS OF DDP IN PRODUCTS

The functions of DDP in the various applications are presented in Table 3. The properties refer to those of 4-DDP (CAS: 27193-86-8), however the properties of the other isomers can be expected to be comparable.

4.3. APPLICATIONS OF TTBP

Applications found for TTBP are listed in Table 4. The STN database was the main source used to compose this list and it is important to mention that many of these applications are extracted from patents. In this manner, some of these applications should be considered as potential applications rather than common applications.

TABLE 4: APPLICATIONS FOR TTBP

APPLICATION FIELD	SPECIFIC APPLICATIONS
An additive in fuel, oil, gasoline or lubricants.[38]	Permissible antioxidant for aviation fuel (when mixed with other butylphenols).[39] An additive to “clean” gasoline.[40]
Chemical intermediate	Starting material for the synthesis of 2,6-di-tert-butyl-4-methoxyphenol which is a powerful antioxidant.[41]
Additive to plastics	An additive to polymeric construction compounds that can be used for flooring or pavement of sports ground.[42] An antioxidant added to polypropylene drainage pipes for trenchless replacement of pipes.[43] Main component of phenolic amino resins used as stabilizing agent for diene rubber.[44] Main component in butylphenols mixture combined with 6-etoxyquinolines mixtures to compose the stabilizer for vulcanized rubber.[45] Rubber stock with good vulcanization rate contains condensation product of TTBP.[46]
Pesticide	A rodenticide of the anticoagulant type.[47]
Other	A component composing the stabilizing agent of an ethylene-vinyl acetate copolymer adhesive.[48] An additive to a processing aid for rubber compounds comprised of vegetable oil, produced from waste.[49] An antioxidant used in latex for carpet-backing coatings, protects the coating but does not discolor it.[50] Stabilizer in jet-recording inks containing cyclohexanone.[51]
Potential use	CO_2-soluble sand binder for production of casting molds.[52]

Several of the applications listed in the tables above are extracted from the STN database and are often quoted from patents. Thereby, the listed applications should be considered as possible/ potential applications for these components.

TTBP is used mainly as a stabiliser added to petroleum based products. However, as listed in the table above the applications are potentially very broad including its use as a pesticide.

The most common products where TTBP is used are:

- Additive to fuel: (anti-oxidants in hydroprocessed fuel)
- Composition of phenolic resins (rubber/ink)

Research within this project was also carried out in order to identify any potential uses in cosmetics or pharmaceuticals. Internet research showed no potential use in these sectors.

5. APPLICATIONS OF THE COMPONENTS IN NORWAY

5.1. DDP AND TTB SPECIFIC APPLICATIONS IN NORWAY

Norway does not produce DDP nor TTBPs and according to the Norwegian Product Register, to date there is no direct import of DDP nor TTBP into Norway. These chemicals are only imported as part of preparations/ products.

The objective of this section is to define the applications of DDP and TTBPs in Norway and thereby identify in what products the chemical will be expected to be found.

To do so, major industrial European and Norwegian actors in the fields of the applications mentioned in Table 2 and Table 4 were contacted.

The answers are gathered in Table 5. For reasons of business confidentiality, the names of the companies contacted are not indicated.

DDP and TTBPs are expected to be found in the following products in Norway:

- Imported fuel, as a potential fuel additive compound
- Crankcase lubricants (automotive and shipping), as an additive compound
- Products composed of phenolic resins: in particular tyre rubber and ink

TABLE 5: DDP AND TTBPS IN NORWAY

APPLICATION IDENTIFIED FOR DDP AND TTBPS	RELEVANT TO NORWAY	NOTE
Additive in fuel, gasoline produced in Norway	No	There are two refineries in Norway and both responded that neither DDP nor TTBPs were used in their processing.
Additive in oil lubricants	Yes	DDP is used in some of these products imported into Norway. A major lubricant supplier in Norway has confirmed that DDP -phenol were found in most of their motor oils.
Additive in imported fuel	Probable source	The addition of TTB or DDP phenols are dependent on the manufacturing process of fuel. Imported fuel may contain the chemicals, however the concentrations are expected to be very low. Norway imports ca. 22% of its annual fuel consumption.
Additive to rubber	Possible in Novalac resins. Tyre rubber is a potential source, but if any in very low concentrations.	The European resin manufacturers association (ERMA) indicated a very low use of DDPs in Novalac resins. TTBP is not used in phenolic resins. The European tyre and rubber manufacturer association (ETRMA) contacted its members as regards to the presence of DDP and TTBP in their products. The few that responded indicated they did not use DDP or TTBP. Contact with one major plastic product producer in Norway indicated that neither DDP nor TTB phenols were present in their products. The tyre manufacturers contacted were not aware of the presence of the chemicals in their products.
Pesticide (seed dressing, pesticide component)	No	Norwegian Food Safety Authority confirmed the components were not authorized in pesticides used in Norway
Paints and varnishes	No	Contact with the 2 main paint producers/importers in Norway: neither use DDPs nor TTBP in their production. Other imported products from minor suppliers could contain the chemicals, however volumes are expected to be low.
Inks	If any, in very low concentrations	Major ink manufacturers were contacted, none were aware of the presence of DDP and TTBP in their products, however they do no intentionally use TTBP or DDP.

5.2. ESTIMATION OF THE TONNAGE IMPORTED INTO NORWAY

From what has been declared to the Norwegian Product Register the tonnage is as follows: Figure 1 and Figure 2 show the trend as regards to the tonnage of 2 DDPs into Norway since 2002. Figure 3 illustrates the import of TTBP. Finally Figure 4 shows the general trend of import of the 3 mentioned chemicals. This shows clearly that the import has decreased since 2002. (The import consists solely of chemicals in formulated/manufactured products.)

As discussed in chapter 5.1 DDP and TTBP are minor components found in the following products:

- Imported fuel: the quantities of the chemicals are very small in the final product and are not indicated on the MSDS. Consequently if fuel additive composed of DDP or TTBP is used in the manufacturing of imported fuel, the corresponding tonnage of the phenols free in the fuel are not expected to be declared to the Norwegian Product Register.
- Crankcase lubricants (automotive and shipping): the presence of DDP is indicated on the MSDS of certain lubricants. Furthermore, one major lubricant supplier in Norway, confirmed using a DDP in the lubricant additive used in the manufacturing of their crankcase lubricants (motor oil), however the chemical is not indicated in the MSDS of the concerned products. MSDS that indicate the presence of DDP, declare an average content of 0.15%, in this manner as long as more than 1 tonne of lubricant is imported, the corresponding tonnage of DDP should be declared to the Norwegian Product Register. However, the tonnage declared to the Norwegian Product Register is expected to be an underestimation of the real import of DDP via crankcase lubricant.
- Phenolic resin in rubber, in particular tyres: when the chemicals are present in the composition of the rubber they will not be declared or registered.

TABLE 6: REGISTERED TONNAGE OF DDPS AND TTBP IN NORWAY

CAS	2009	2008	2007
27193868	0,029	0,02	0,02
74499357	0,001	*	*
121158585	0,18	0,25	0,44
732263	0,22	0,31	0,88
Total	**0,434**	**0,58**	**1,34**

* *Information was not available for 2007 and 2008.*

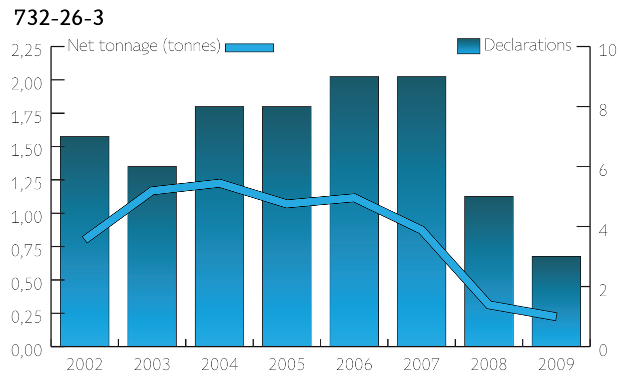


Figure 1 Registered DDP, CAS 27193-86-8

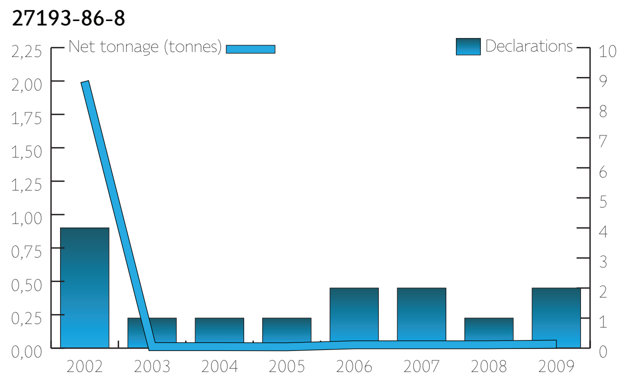


Figure 2 Registered DDP, CAS 121158-58-5

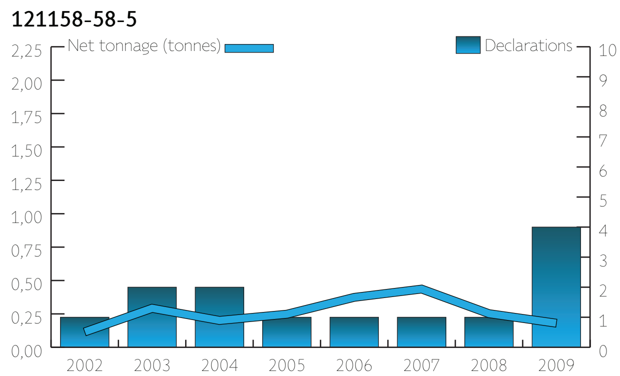


Figure 3: Registered TTBP

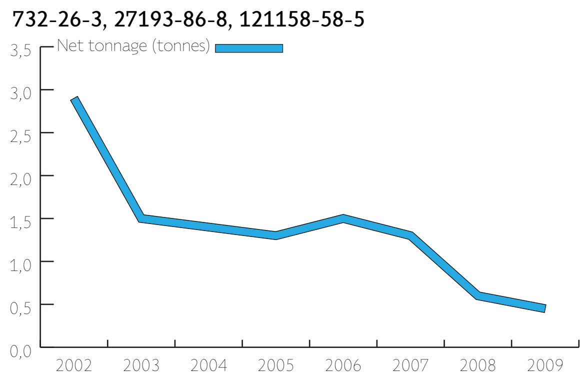


Figure 4: Total registered DDPs and TTBP in Norway

In conclusion, the tonnage registered in the Norwegian Product Register is expected to be an underestimation of the factual import of DDPs and TTBP in products. The following chapter will attempt to address this underestimation and quantify the potential import of the chemicals. It is however important to note that to date, there is no clear record as regards to the content of the chemicals in products and what percentage of each product group is likely to contain the chemicals. Thereby the following estimations are based on assumptions and in particular on "worst case" scenarios.

5.2.1. Import of TTBP via fuel

According to the 2009 statistics provided by Statistics Norway (SSB) (see Table 7), the import of fuel into Norway represents 22% of the national consumption.[53] Neither DDP nor TTBPs are used in the manufacturing of domestic oil refineries and is only used in refineries that use hydrotreating as their process mechanism. According to the Additives Technical Committee (ATC) the use of TTBP has been reduced in the last five years.[54] However, it is not possible to determine the percentage of imported fuel manufactured by hydrotreating process using TTBP. In order to estimate the potential import of TTBP into Norway via fuel, it will be assumed that all fuel imported contains TTBP as an additive. This is the worst case scenario.

According to a major jet fuel manufacturer, to date there are 6 additive packages authorized for the use in aircraft (civilian and military). One out of the six preparations contains TTBP. The composition of the antioxidant mixture is as follows:

- 75 % minimum, 2,6 ditertiary-butyl phenol
- 25 % maximum mixed tertiary and tritertiary butyl-phenols

According to the same source, the maximum dosage of this additive package into fuel is 24 mg/l.

Dosages of TTBP in the additive and the dosage of additive in fuel is expected to vary specifically to the type of fuel manufactured, however the differences are not expected to be extremely high. In this manner, in order to estimate the potential import of TTBP into Norway via fuel, the dosage rates known for aviation will be applied for all fuel imported.

TABLE 7: AUTOMOTIVE FUEL STATISTICS 2009[55]

PRODUCTION	4 113 000 tonnes
CONSUMPTION	1 271 000 tonnes
IMPORT	285 000 tonnes
EXPORT	2 743 000 tonnes

(The numbers do not add up, as some of the fuel produced in Norway is stored).

FACT BOX: THE NORWEGIAN PRODUCT REGISTER:
The Product Register is the official central register of chemical products traded in Norway. All chemical products classified in regulation on classification and labelling of dangerous chemicals and produced or imported in volumes above or equal to 100 kg, must be declared to the Product Register. The declaration duty extends to products covered by the regulation on declaration and labelling of microbiological products and by the regulation on biocides.

WORST CASE SCENARIO ESTIMATION - IMPORT OF TTBP VIA FUEL

Maximum mixed tertiary and TTBP in antioxidant mixture	25%
Fuel density	0,74 kg/l
Maximum dosage of antioxidant in fuel	24,0 mg/l = 0,0032%
Maximum dosage of TTBP in fuel	0,0008 %
Import of car fuel (2009)	285 000 tonnes
Import of jet fuel (2009)[56]	181 571 tonnes
Total import of TTBP via fuel	**3,73 tonnes**

The result is higher than the total tonnage registered in the Norwegian Product Register, the tonnage is expected to be an overestimate.

DDP are not reported to be used as a fuel additive in Norway and do not enter the composition of any jet fuel additive. Furthermore, the 2007 UK Study on C12-alkyl-phenols does not consider fuel as a source of DDP. Consequently, in this report fuel additive will not be considered as a source of DDP. If any, the quantities will be small.

5.2.2. Import of DDP via crankcase lubricant

Norway does not produce lubricant additive packages or lubricants, all hydrocarbon based lubricants are imported.

The 2007 UK study,[57] states that C12-alkyl-phenols are used in crankcase lubricants and in marine lubricants. The remaining content of unreacted DDP in the final product is minor.

The content of DDP in lubricants known to be imported into Norway compose below 1% of the lubricant. The following calculations will use an average DDP content of 0,2% by weight, this is based on information supplied by lubricant manufacturers.

According to information gathered from lubricant suppliers to Norway, TTBP does not appear to be used as an additive; however the Canadian study does indicate that TTBP has been used in the past in lubricants. Nevertheless, DDP will be the most common of both chemicals potentially found in lubricants and in this manner the import of TTBP via lubricants will be considered as a minor import route for the chemical. Hence, the following estimations are based on data relative to DDPs only.

Sales of lubricant oil in Norway, in 2006 accounted for 70 000m^3. However, DDP will be expected to be found only in crankcase lubricants (motor oil for automotive and marine purposes). According to Table 8, the import of motor oils, compressor oils and turbine oils to Norway in 2009, accounted for 25089 tonnes.

A complete survey of the market shares for motor oils containing DDP has not been made, but according to a major supplier of motor oils to both large and small vehicles, about 15% of their products contain DDP. Thereby the total tonnage calculated here is expected to be overestimated.

WORST CASE SCENARIO ESTIMATION - CRANKCASE LUBRICANTS

Average content of DDP in crankcase lubricants	0,2%
Import of motor oils, compressor oils and turbine oils, 2009	25089 tonnes
Worst case scenario: import of DDP via crankcase lubricants	**50 tonnes**

5.2.3. Import via phenolic resins: tyre rubber

Phenolic resins are oligomers synthesized by repeatedly linking phenolic monomers with aldehyde chemicals. Today, there are a wide range of reaction conditions and monomers available to produce a variety of resins specifically designed for use in individual applications. There are two general resin types: NOVOLAC resins and RESOL resins.

Phenolic resin effortlessly penetrates and adheres to the structure of many organic and inorganic fillers and reinforcements, which makes it an ideal candidate for various end uses.[59]

The properties of phenolic resins are:

- hardness;
- heat resistance: they withstand high temperatures under mechanical load with minimal deformation or creep;
- chemical resistance: they provide an impervious shield to protect a variety of substrates from the corrosive effects of chemicals.

According to the European Resins Manufacturers Association (ERMA)[60], TTBP is not used in phenolic resins and very little DDP is used. DDP would be added mainly to Novalac resins, in order to modify the properties of the resin according to specificities desired. Tyres and technical rubber goods use straight phenolic Novolac resins as reinforcing agents.

A few members of the European Tyre and Rubber Manufacturer Association (ETRMA) indicate they do not use DDPs.

The import of automotive tyres to Norway represented a total of 43 000 tonnes in 2009.[61] There are no other areas of use for rubber that can compare to this tonnage. However one major pipe manufacturer in Norway was contacted and confirmed that neither DDP nor TTBP were used in the manufacturing of their products. In this manner in this report, the use of phenolic resin will only be assessed for its use in tyres.

TABLE 8: IMPORT OF LUBRICANT TO NORWAY, PER CATEGORY OF LUBRICANT (TONNES) [58]

TRADE NUMBER AND TYPE	2002	2003	2004	2005	2006	2007	2008	2009
27101981 Motor oils, compressor oils and turbine oils	22136	19244	22437	22170	23305	24169	26825	25089
27101983 Hydraulic oils	5146	5961	5647	4869	6680	7841	8632	8906
27101985 White oils	261	2449	5590	2279	3424	6649	5827	5648
27101987 Gear oils	2241	2423	2660	2523	3191	4226	4973	5262
27101991 Metalworking oils, form oils and rust protection oils	771	827	1355	5232	2125	1626	1597	1077
27101993 Insulation oils	156	26	184	117	502	798	1353	773
27101994 Lubricants	41042	37165	35243	29946	23773	25689	18953	11611

The content of unreacted DDP in tyre rubber is expected to be low and according to the information provided by European manufacturer associations the use of the DDP does not appear to be common. However this application shall be discussed in this report in order to illustrate the potential import and emission via phenolic resins, which appears to be the second most common application of DDPs.

According to the 2007 UK study,[63] resins are generally added to rubber in amounts up to 1,5% of the rubber formulation. The maximum concentration of free para-C12-alkylphenols in the resins used to make tyres is assumed to be 3%. In this manner free para-C_{12}-alkylphenols will represent 0,045% of the rubber composing the tyre. According to the data reported by ETRA, in Table 9, rubber composes 43 – 48% of a tyre, consequently free para-C12-alkylphenols will represent 0,02% of the tyre. The proportion of DDP amongst the para-C_{12}-alkylphenols present is difficult to estimate, consequently in this report the data for para-C_{12}-alkylphenols will be directly used for DDPs. This is obviously an overestimate.

The worst case scenario would be to consider that all tyres imported contain DDP or TTBP.

TABLE 9: THE COMPOSITION OF TYRES IN THE EUROPEAN UNION: MATERIAL PASSENGER CARS TRUCKS/ BUSES[62]

MATERIAL	CONTENT
Rubber /Elastomers	43 % - 48 %
Carbon black	21 % - 22 %
Metal	15 % -27 %
Textile	5 %
Zinc oxide	1 % -2%
Sulphur	1 %
Additives	6 % - 8%

WORST CASE SCENARIO ESTIMATION - TYRES

Free para-C12-alkylphenols (DDP) in a tyre	0,02%
Import of tyres in 2009	43 000 tonnes
Worst case scenario: import of DDP via tyres	**9,6 tonnes**

5.2.4. Import via phenolic resins: Ink

As mentioned in earlier, the presence of DDP and TTBP are not expected to be significant in inks, this is further discussed in this section.

Printing inks are made of four basic components:

- Pigments
- Resins
- Solvents
- Additives

Resins bind the other ingredients of the ink together so that it forms a film and they bind the ink to the paper. They also contribute to gloss and resistance to heat, chemicals and water.

Different resins will be used according to the application of the ink and typically more than one resin is used in a given ink. Phenolic resins count among the most commonly used resins. According to CEPAD (UK study), printing inks account for resins produced from para- C_{12}-alkylphenols.

The manufacturing of ink is divided in two stages:
Varnish manufacturing: ink varnish, drying oil, alkyd and other solvents are added to the vessel under nitrogen prior to cooking. Hard resins are then added when the correct temperature is attained. The cooking process continues until the reactants are either totally consumed in the transesterification process or achieve adequate solubility in the solvent. The additives are added after the batch cools down.

Pigment dispersal: pigments are added to the varnish.

The manufacturing of inks requires high temperatures, any free DDP or TTBP from the phenolic resin is expected to be mostly consumed in this process and very low concentrations are expected to be detected in the final ink. The 2007 UK study,[64] also states that no significant traces of para-C_{12}-alkylphenols are left in the finished inks. This correlates with the fact that ink manufacturers are not aware of the presence of neither DDP nor TTBP in their products.

Hence releases from the printing process, or from the recycling of paper printed with these inks, are negligible and will not be discussed in this report.

6. EMISSION OF DDP AND TTBP

DDP and TTBPs are neither produced nor handled as "pure chemicals" in Norway, they are minor components in a limited number of products. Accordingly, their emission in the environment is expected to be low. The following chapter addresses the environmental behaviour of the chemicals and discusses their potential emission routes in Norway, as well as highlights eventual methodologies to estimate their environmental emission.

6.1. EXPECTED ENVIRONMENTAL BEHAVIOUR

6.1.1. Environmental behaviour of DDP[65]

The following information is based on data gathered for the isomer CAS: 27193-86-8 on the HSDB database (Hazardous Substances Data Bank operated by the US National Library of Medicine). Similar characteristics are expected from the other DDP isomers.

Estimated Koc = 90 000
Vapor pressure = 6,93.10-5 mm Hg at 25 deg C

Fate in the hydrosphere:

Based on the partition coefficient carbon/water (Koc), DDP is expected to partition from the water column to sediment and suspended material and be strongly adsorbed.

The volatilization properties of DDP suggest that in the absence of strong adsorption, volatilization may be a viable transport process.

Fate in the atmosphere:

DDP is expected to exist primarily in the vapour-phase in the ambient atmosphere, although some may also exist in the particulate-phase.

Particulate-phase DDP can be physically removed from air by wet and dry deposition processes.

Vapor-phase DDP half-life in the atmosphere by reaction with photochemically induced hydroxyl radicals: $T_{1/2}$ = 3.7-6.65 hr

Night-time reaction with nitrate radicals may also contribute to the atmospheric removal of the vapour-phase.

Fate in soil and sediment:

Based on the partition coefficient carbon/water (Koc), DDP is expected to be immobile in soil.

In conclusion, DDPs are expected to partition mainly to soil/sediment, where they shall persist and may be available to bioaccumulate in organisms.

6.1.2. Environmental behaviour of TTBP[66]

The following information is based on data available on the HSDB database for TTBP.

Vapor pressure = 6.61X10-4 mm Hg at 25 deg C
Estimated Koc = 63,000
Estimated Henry's Law constant = 6.5X10-6 atm-cu m/mole

Fate in the hydrosphere:

Based on the partition coefficient carbon/water (Koc), TTBP is expected to adsorb to suspended solids and sediment.

The Henry's law constant suggests that volatilization from water is expected to be an important fate process but will be attenuated by adsorption to suspended solids and sediment in the water.

Fate in the atmosphere:

The vapour pressure of TTBP indicates that the component will exist in both the vapour and particulate phases in the atmosphere.

Half-life of the atego-phase by reaction with photochemically-induced hydroxyl radicals: $T_{1/2}$= 24 hr
The particulate-phase will be physically removed by wet or dry deposition.

TTBP is not expected to be susceptible to direct photolysis by sunlight.

Fate in soil/sediment:

Based on the partition coefficient carbon/water (Koc), TTBP is expected to be immobile in soil.

TABLE 10:
TTBP PARTITIONING INTO EACH COMPARTMENT (%) [67]

SUBSTANCE RELEASED TO:	AIR	WATER	SOIL	SEDIMENT
Air (100%)	0	0	100	0
Water (100%)	0	2	4	94
Soil (100%)	0	0	100	0

The Henry's law constant suggests that volatilization from moist soil surfaces is expected to be an important fate process.

The following table indicates the expected partition of TTBP based on the results of an equilibrium criterion model by Environment Canada.

In conclusion, TTBP will mainly partition to soil/sediment, where it shall persist and may be available to bioaccumulate in organisms.

6.2. STUDIES LOOKING INTO THE ENVIRONMENTAL EMISSION OF DDP AND TTBP

The environmental emissions of DDP and TTBPs have been little studied. To date, 4 studies have been found:

UK:[68] *Environmental risk evaluation report: para-C_{12}-alkylphenols(dodecylphenol and tetrapropenylphenol, 2007*

This risk assessment covers any branched chain para-C_{12}-alkylphenol in commercial use in Europe, but particularly "phenol, (tetrapropenyl) derivatives" (CAS no. 74499-35-7) (tetrapropenylphenol) and "dodecylphenol, mixed isomers (branched)" (CAS no. 121158-58-5). Overall, the assessment identifies potential environmental risks from production, use as an intermediate, and most end-uses of the derivatives and resins (which all contain some para-C_{12}-alkylphenols as impurities).

The methodologies used to describe the emissions of para-C_{12}-alkylphenol can be transposed to the emissions of DDP and TTBPs in Norway by making a few adjustments to national conditions.

SWEDEN:[69] *Screening tertiary butylphenols, methylphenols, and long-chain alkylphenols in the Swedish environment, IVL Rapport/report B1594, 2003*

A screening study of 30 phenolic compounds is presented, covering 14 tertiary butylphenols and related substances, 7 methylphenols and 9 long-chain (C_8, C_9, C_{12}) alkylphenols, including DDP. The main objectives of the study were to determine environmental concentrations of these substances in a variety of environmental media in Sweden, to highlight important source categories, and to link the environmental occurrence to the current use in Sweden.

No methodology was established to estimate the emissions, but the results of the environmental screening are interesting to compare to estimated emissions.

CANADA:[70] *Screening assessment of the challenge: phenol 2,4,6-tris(1,1-dimethylethyl) – (2,4,6-tri-tert-butylphenol), CAS 732-26-3, 2010*

Risk assessment carried out, looking into the applications of TTBP in Canada and estimating the emission into the environment in order to estimate the risk associated to the use of this component in Canada. Only one application was identified in Canada; additive in fuel. The methodology used to estimate the emissions in this study can be easily transposed to Norway.

US EPA:[71] *An exposure and risk assessment for phenol, EPA-440/4-85-013, 1981*

Risk assessment of alkyl phenols in 1981 in the US. This study looked into the use of DDP in the use and the related emission. However the only application identified and looked into was lubricant production. As there is no lubricant manufacturing in Norway, the methodology is not of interest here.

NORDIC SCREENING GROUP:[72] *TemaNord 2008:530: Screening of phenolic substances in the Nordic environments, 2008*

Screening was carried out in all Nordic countries and analysed for different phenols, amongst which DDP. There is no estimation as regards to the emission, but the results of the screening will be a useful tool to compare the theoretical emissions associated to the applications of DDP in Norway with the actual contents found in the environment.

SSB:[73] *Use and emissions of hazardous substances in Norway, 2002-2007, 2009*

Statistics Norway has in recent years published statistics of use and emissions of hazardous substances in Norway. The latest covers the years 2002 through 2007. The statistics covers 450 substances categorized as being CMR (Holmengen). Of these 450 substances, three are of interest for this project, CAS-numbers 27193-86-8, 121158-58-5 and 732-26-3. The emissions are calculated by multiplying amount used of each substance by an emission factor. The amount used is the sum of import and production minus export. The numbers are from the Norwegian Product Register. Emission factors are gathered from several sources and the accuracy varies.

6.3. POTENTIAL EMISSIONS OF DDPs AND TTBP IN NORWAY

This chapter will look into the emission of DDP and TTBP in Norway. The emission scenarios discussed in this section are expected to be the most significant, nonetheless these are likely to not be the only ones.

The scenarios considered are:

- use and disposal of fuel in Norway
- use and disposal of oil lubricants in Norway
- use and disposal of tyres in Norway

6.3.1. Emission from fuel additive

In order to estimate the potential emissions from the use of DDP and TTBPs as fuel additives, the 2009 Canadian study[75] has established a clear methodology to do so. In this section the methodology, assumptions and estimates indicated in the Canadian study will be directly transposed to Norwegian consumption of TTBPs as additives in fuel.

Manufacturing of fuel: blending of the additive package with the fuel; could be a potential source of emission. However there are two crude oil refineries in Norway: Mongstad and Slagentangen and both refineries have confirmed that neither DDP nor TTBPs are used in their manufacturing.

By using the worst case scenario it has been assumed that the total import of TTBP via fuel= 2,3 tonnes / year.

The 2009, Canadian study on TTBP used models to estimate the emissions of TTBP into the environment. First it was assumed that the substance behaves similarly to gasoline when used as a fuel additive. Based on existing regulations and a worst-case scenario, it was assumed that loss by transformation during combustion is 99,6%.

Table 11 and Table 12 estimate the potential environmental emission of TTBP via fuel combustion and its partition in the different environmental compartments. The results are according to the worst case scenario and are expected to be an overestimate.

TABLE 11: ANNUAL EMISSION OF TTBP FROM FUEL COMBUSTION

Transformation of TTBP during combustion	99,60 %
TTBP emitted during combustion	0,40 %
Worst case scenario: Import of TTBP via fuel	3,73 tonnes
Worst case scenario: Total TTBP emitted	**15 kg**

TABLE 12: ENVIRONMENTAL PARTITION OF TTBP EMISSION FROM FUEL COMBUSTION

ENVIRONMENTAL PARTITION	% ACCORDING TO THE 2009 CANADIAN STUDY	EMISSION OF TTBP (KG)
Water	15,0 %	2,75
Air	80 %	12
Soil	5 %	0,75

6.3.2. Emission from crankcase lubricant additives

Assuming the worst case scenario considered in the estimation of the import of DDP via lubricants, a total of 50 tonnes of DDP could potentially be imported. Marine lubricants used in two-stroke engines will be burnt with the fuel. There will be no emission of DDP related to this use.

On the other hand, crankcase oil for automotive use (motor oil) for four-stroke engines will not be burnt with the fuel.

WORST CASE SCENARIO ESTIMATION FOR DDP IN CRANKCASE LUBRICANT ADDITIVE

Worst case scenario: DDP imported via motor oil	25 tonnes
Worst case scenario: DDP remaining in waste motor oil	12,5 tonnes
Worst case scenario: DDP in Motor oil not disposed properly	**3,76 tonnes**

According to the 2007 UK-study, half of the content of DDP in lubricants will be destroyed during the oils lifetime, in this manner 25 tonnes of DDP will be potentially found in waste oil. Klif's "Environmental Status" states that to date, 85% of waste oil is collected and managed appropriately.[74]

3,8 tonnes of DDP have an unknown fate and are potentially released directly into the environment or into collective waste water systems.

However this is the worst case scenario and is expected to be an overestimation of the real emissions. The emission calculated here is well above the declared amount in the Norwegian Product Register.

Both the UK and Canadian study, consider the potential emission of chemicals from the remaining content of lubricant in disposed containers. In Norway, these containers are meant to be disposed as "hazardous waste" and will be managed appropriately. However it is expected that some of these containers will be disposed with "household waste". In Norway household waste is incinerated and thereby, the emission of these chemicals is not expected to occur to any significant degree. Hence, this emission route is not considered in this report.

6.3.3. Emission from tyres in Norway

The 2007 UK study[76] addresses the potential emission of para-C12-alkylphenols in tyres. The methodology used for the UK can be transposed and adapted to Norwegian conditions. Both the emissions in use and at disposal is discussed in this chapter.

At present, there is no manufacturing of tyres in Norway, all tyres are imported and the only potential emission of DDPs from tyres can only occur during their use and disposal.

Emission in use

Loss from tyres in use is expected to occur through abrasive wear of the material rather than through leaching or volatilisation. The 2007 UK study[77] gathered information documenting that the resin potentially containing the phenols of interest, is used in the interior portion of the tyre and is thereby not expected to be subject to abrasion and loss during use. However there are also indications that a related substance to DDPs (4-tert-octylphenol) has been found in road runoff. In this manner the 2007 UK Study[78] suggests to discuss this emission route, however recognizing that "it might not be wholly realistic for para-C_{12}-alkylphenols".

The potential emission of DDP through the abrasion of tyres will follow the methodology used by the UK using specific Norwegian data and further detailed.

The metal and textile content of the tyres will not be expected to compose the material that will undergo abrasive wear during tyre use. It will be considered here that all the other components, including free DDPs will be subject to abrasive wear and at the same rate.

Average weight reduction over a tyre's life-span= 16%, regardless of the vehicle category.

According to the 2007 UK study,[80] resins are generally added to rubber in amounts up to 1,5% of the rubber formulation. The maximum concentration of free para-C_{12}-alkylphenols in the resins used to make tyres is assumed to be 3%. In this manner free para-C_{12}-alkylphenols will represent 0,045% of the rubber composing the tyre. As the rubber composes ca. 60% of what will be loss during the life-span of the tyre, the free para-C_{12}-alkylphenols will compose 0,027% of the loss. It will be assumed that free para-C_{12}-alkylphenols is equal to the quantity of free DDPs.

To date, no data has been found as regards to what percentage of tyres sold in Norway contain DDP. The worst case scenario is to consider that all tyres in Norway contain DDP. As indicated in Table 15, considering the worst case scenario, a maximum of 2,6 tonnes of DDP will be emitted to the environment via the use of tyres. However, the environmental availability of the phenols in abraded tyre is also subject to reserve.

The release is assumed to be split equally between surface water and soil (e.g. roadside).

In conclusion, this route could be a significant source of emission of DDP, however it is not realistically expected to be of much significance, as its use in phenolic

TABLE 13: TYRE LIFE-SPAN WEIGHT REDUCTION IN NORWAY (KG)[79]

AUTOMOBILE CATEGORY	WEIGHT NEW	USED TYRES (at disposal)
Car	± 9 - 11	± 7 - 9
Van	± 11 - 15	± 9 - 11
Truck	± 50 - 80	± 40 - 70
Tractor	± 100	± 85

TABLE 14: TOTAL COLLECTED TYRES IN NORWAY IN 2008[81]

Tyres collected	50 695 tonnes
Including c.a. 4,5 % water/ice/other waste	2 420 tonnes
Tyres collected, net weight	48 275 tonnes

TABLE 15: ANNUAL POTENTIAL EMISSION OF DDPs AND TTBP THROUGH TYRES USE

Annual disposal of tyres (2008)	48 275 tonnes
Equivalent in new tyres (before 16% loss)	60 351 tonnes
Estimated annual tyre loss through use (abrasion)	9 656 tonnes
Worst case scenario: Total loss of DDP via abrasive wear of tyres	2,6 tonnes

TABLE 16: KEY STATISTICS 2008, RECYCLING OF TYRES

RECYCLING	STATISTICS FOR 2008[82] (TONNES)	EXPECTED EMISSIONS
Energy: Cement production	9 528 tonnes	As in car fuel, DDPs are expected to be destroyed at high temperatures. If any DDP or TTBP is emitted to the air, it is expected to be in very low rates and the chemicals have a short half-life in the atmosphere.
Recycled material for civil engineering	26 737 tonnes	A risk assessment of 4-tertoctylphenol looked into the leaching of the substance from tyre residues after disposal and recycling and concluded that overall emission of the chemical through this route was likely to be negligible. Para-alkyl- C12-phenols are used in much lower level than that of 4-tert-octylphenol, thereby emissions are expected to be insignificant.
Blasting mats	1 755 tonnes	Expected to undergo significant, damage and abrasion in use, which is difficult to estimate. However this source is not expected to be a major contributor to the presence of DDPs in the environment.
Silages	1 616 tonnes	No emission is expected, since leakage or volatilisation is not expected to occur.
Reuse/export (retreaded)	1 787 tonnes	Potential emission from tyre abrasion.
Fenders for docks and other (e.g. playground equipment)	462 tonnes	The components of interest are not expected to leach out of the rubber into the water. The abrasion is not expected to be comparable to that of tyres on the road. Very old rubber can potentially disintegrate, however the environmental availability of DDPs in the disintegration material is expected to be low.[83]
Waste	2 420 tonnes	Expected to be burnt in an incinerator. No emissions of DDP or TTBPs are expected.

resins is low.

Emission at disposal:

In Norway all old tyres are collected and transported to either Kjøpsvik or Skjerkøya, where the tyres are sorted and recycled as indicated in Table 16.

In conclusion, emissions of potential DDPs from disposed/recycled tyres are expected to be very low.

6.3.4. Emission estimation: SSB methodology

The methodology used by SSB to estimate the emissions are calculated by multiplying amount used of each substance by an emission factor. The amount used is the sum of import and production minus export. The numbers are from the Norwegian Product Register. There are four groups of emission factors, reflecting the level of knowledge, and thereby the level of uncertainty:

1. Factors specific for combinations of substance (CAS), product type (UCN) and industrial sector (NACE)
2. Factors specific for combinations of product type and industrial sector
3. Factors specific for product type
4. General emission factor

The emission categories range from 1 – 4, 1 is the most certain. This is an emission factor for products with large volumes and is set specifically after consulting the industry. For sector or product types unknown, the emission category is 4 and the emission factor is set to 1 for a worst case scenario (Holmengen).

TABLE 17: EMISSION OF DDP AND TTBP ACCORDING TO THE SSB METHODOLOGY[84]

CAS NR.	PRODUCT TYPE	CONSUMPTION (TONNES)	EMISSION FACTOR	EMISSION (TONNES)
27193-86-8	R10990	0,001809600	0,000100	0,00000018096
27193-86-8	B60200	0,028006000	0,002500	0,000070015
74499-35-7	S45180	0,001131260	0,500000	0,00056563
121158-58-5	M05443	0,058310000	0,100000	0,005831
121158-58-5	S45180	0,002000000	0,500000	0,001
121158-58-5	M05243	0,027000000	0,100000	0,0027
121158-58-5	M08100	0,093100000	0,500000	0,04655
732-26-3	S45300	0,001213905	0,500000	0,0006069525
732-26-3	B55200	0,034908545	0,000005	0,000000174542725
732-26-3	P15400	0,187460000	0,100000	0,018746
Total DDP emission				**0,056717**
Total TTBP emission				**0,019353**

6.4. PRESENCE OF DDP IN THE NORDIC ENVIRONMENT

The presence of DDP in the environment has been carried out recently in the Nordic countries, by the Nordic council[85]. All six Nordic countries participated in the project that included the sampling and analysis of 120 samples from different environmental compartments.

The samples included the following:

WATER SAMPLES: waste water (influents and effluents) from sewage treatment plants (STPs) and effluents from landfills; surface run-off and recipient water samples from both freshwater/brackish and marine environments.

SOLID SAMPLES: sewage sludge from STPs, soil from landfills and sediments from both marine and freshwater environments.

BIOLOGICAL SAMPLES: mussels from marine environments, fish from both freshwater/brackish and marine environments, marine mammals (seal and pilot whales) and two egg samples from seabirds (black guillemots). DDP was amongst the phenols found in the highest concentrations in all sewage water samples, with higher concentrations in the effluent than the influent of the STP, see results in Table 18. DDP was detected in fish and mussels.

The presence of DDP in sewage water could be linked to the disposal of crankcase lubricants.

TABLE 18: SCREENING RESULTS OF DDP IN STPS IN NORWAY[86]

CONCENTRATION OF DDP IN SEWAGE SLUDGE FROM STPS, 2006/2007 (µg/kg dw)				CONCENTRATION OF DDP IN STPS, 2006/2007 (ng/l)			
BEKKELAGET		OSLO VEAS		BEKKELAGET		OSLO VEAS	
Wet	dry	silo	wet	effluent	influent	effluent	influent
47 396	17 492	11 334	47 021	-	2154	1294	1356

7. CONCLUSION

The objective of this report is to technically support the emission reduction aimed for by Norway, by documenting where and how reductions could potentially be carried out specifically for TTBP and DDPs. According to chemical manufacturers the production of TTBP and DDPs has been reduced within the last five years, consequently the use of the chemical is expected to have been reduced. This correlates with the reduction registered in the Product Registry.

Neither TTBP nor DDPs are produced or imported as pure chemicals to Norway. These compounds will exclusively be imported via products.

In Norway, TTBP is expected to be used as an antioxidant in fuel produced by hydrotreating. Only imported fuel will potentially contain traces of TTBP and will not be registered in the Norwegian Product Register.

DDPs are expected to be used mainly as an additive in crankcase lubricant manufacturing. Not all suppliers indicate the content of DDP, though it is used in their manufacturing. The registered tonnage in the Norwegian Product Register is expected to be an underestimation of the real import via lubricants.

DDPs are also used in the manufacturing of phenolic resins. Though this is not a common practice DDPS are expected to be found in certain phenolic resins and in particular in Novalac resins. The final concentration of DDP in the final product (e.g. rubber, ink) will be very low. The main import of free DDP via phenolic resins is expected to occur via tyres.

DDP and TTBP are minor components in products. The total tonnage registered in the SPIN database is expected to be an underestimate. In order to estimate the imported tonnage, precise data is required from manufacturers and importers, and this was not available for this report. The report estimates worst case scenarios of the potential tonnage imported to Norway and are expected to be overestimates.
The emission of the chemicals into the Norwegian environment is limited to the use and disposal of a restrained number of products.

The emissions of the chemicals has been little studied, however methodologies have been designed to give a gross estimate. In this report worst case scenarios have been systematically used to estimate emissions. According to the estimates established, the potential emission of DDP via the abrasive wear of tyres could be the main contributor to the environmental emission of this component, however the actual presence of DDP in tyres is difficult to determine and the environmental availability of the chemical in the abrased material is very uncertain. The non-controlled disposal of motor oil is expected to be the major contributor to the environmental emission of DDP. This correlates well with screening results in the Nordic countries that show that DDP is found in significant quantities in Norwegian STPs. The emission of TTBP via its use in fuel is expected to be insignificant.

In conclusion there is little environmental concern as regards to the presence of TTBP in products in Norway. However, as regards to DDPs, their presence appears to be common in crankcase lubricants and the emission via uncontrolled disposal of engine oil could be of significant environmental concern.

REFERENCES

1. Miljøstatuts website, published by Klima- og forurensningsdirektoratet, 24.02.2010, Prioritetslisten, consulted 04/10/2010
http://www.miljostatus.no/Tema/Kjemikalier/Kjemikalielister/Prioritetslisten/

2. ESIS database: CAS 104-43-8, consulted in October 2010
http://ecb.jrc.ec.europa.eu/esis/

3. ESIS database: CAS 11067-80-4, consulted in October 2010
http://ecb.jrc.ec.europa.eu/esis/

4. ESIS database: CAS 27193-86-8, consulted in October 2010
http://ecb.jrc.ec.europa.eu/esis/

5. Pubchem database: CAS 57427-55-1, consulted in October 2010
http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?cid=22833446

6. DEFRA UK, website, consulted November 2010
http://www.defra.gov.uk/environment/quality/chemicals/ukrisk.htm

7. US EPA, IRIS database: CAS 121158-58-5, consulted in October 2010
http://www.tradingchem.com/Phenol_dodecyl-_branched/121158-58-5.html

8. Pubchem database: CAS 210555-94-5, consulted in October 2010
http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?cid=22833471&loc=ec_rcs

9. HSDB database: CAS 732-26-3, consulted in October 2010
http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB

10. Nordic Council of Ministers, 2008, TemaNord 2008:530: Screening of phenolic substances in the Nordic environments, Nordic Council of Ministers publication, ISBN 978-92-893-1681-1

11. Asger B. Hansen and Pia Lassen, 2008, Screening of phenolic substances in the Nordic environments, TemaNord 2008:530, Nordic Council of Ministers publication, ISBN 978-92-893-1681-1

12. Environment Canada – Health Canada, 2008, Screening assessment of the challenge: phenol 2,4,6-tris(1,1-dimethylethyl) – (2,4,6-tri-tert-butylphenol), CAS 732-26-3
http://www.ec.gc.ca/Publications/default.asp?lang=En

13. Environment agency (UK), 2007, Environmental risk evaluation report: para-C12-alkylphenols(dodecylphenol and tetrapropenylphenol, Environment agency publication, ISBN: 978-1-84432-789-8
http://publications.environment-agency.gov.uk/pdf/SCHO0607BMVN-e-e.pdf

14. Elliott Petroleum LTD, 2006, MSDS: AFX oil anti-freeze

15. Elliott Petroleum LTD, 2008, MSDS: Hydra Blue MG 36

16. MOL-LUB Lubricant Production Trade and Service Limited Liability Company, 2008, MSDS: MOL Transfluid TO-4 SAE 10W

17. OK-Q8 AB, 2009, MSDS: Q8 T 500

18. Total Norge AS, 2009, MSDS: FIRST 500 C2 5W-30

19. Total lubricants, 2006, MSDS: TALUSIA HR 70

20. Exxon Mobil,2010, MSDS: MOBILGARD HSD 15W-40
http://www.msds.exxonmobil.com/psims/psims.aspx

21. Kirk-Othmer Encyclopedia of Chemical Technology: ALKYLPHENOLS, Copyright John Wiley & Sons, Inc., vol 2, p 203-
http://www.scribd.com/doc/30132752/Alkylphenols

22. Kirk-Othmer Encyclopedia of Chemical Technology: ALKYLPHENOLS, Copyright John Wiley & Sons, Inc., vol 2, p 203-
http://www.scribd.com/doc/30132752/Alkylphenols

23. Kirk-Othmer Encyclopedia of Chemical Technology: ALKYLPHENOLS, Copyright John Wiley & Sons, Inc., vol 2, p 203-
http://www.scribd.com/doc/30132752/Alkylphenols

24. Kirk-Othmer Encyclopedia of Chemical Technology: ALKYLPHENOLS, Copyright John Wiley & Sons, Inc., vol 2, p 203-
http://www.scribd.com/doc/30132752/Alkylphenols

25. Kirk-Othmer Encyclopedia of Chemical Technology: ALKYLPHENOLS, Copyright John Wiley & Sons, Inc., vol 2, p 203-
http://www.scribd.com/doc/30132752/Alkylphenols

26. Kostyuchenko, V. M.; Panov, E. P.; Shvarts, A. G.; Pruzhanskaya, N. A.; Vasil'evykh, N. Ya.; Fateeva, G. V., 1977, Rubber mixture based on synthetic rubber, Fr. Demande publication, 20 pp

27. Environment agency (UK), 2007, Environmental risk evaluation report: para-C12-alkylphenols(dodecylphenol and tetrapropenylphenol-Science, ISBN: 978-1-84432-789-8

28. Yang, Quanhai, 2009, Process for producing alkyl phenolic resin for thermoplastic thickener of rubber, Faming Zhuanli Shenqing Gongkai Shuomingshu publications, 23pp.

29. Andrei, Constantin; Micu, Horia; Nitu, Ion, 1990, Elastomers containing antioxidant-fungicides for waterproof coatings for construction , Institutul de Tehnologie Chimica, S.C. ITEC, S.A., Brazi, Rom., Rom. publication, 3 pp.

30. Damo, Zoltan; Neuenschwander, Ernst, 1989, Stabilization of seed dressing emulsions by phenols and saturated and unsaturated alcohols, Eur. Pat. Appl.publication, 8 pp.

31. Kirk-Othmer Encyclopedia of Chemical Technology: ALKYLPHENOLS, Copyright John Wiley & Sons, Inc., vol 2, p 203-
http://www.scribd.com/doc/30132752/Alkylphenols

32. Environment agency (UK), 2007, Environmental risk evaluation report: para-C12-alkylphenols(dodecylphenol and tetrapropenylphenol, Environment agency publication, ISBN: 978-1-84432-789-8
http://publications.environment-agency.gov.uk/pdf/SCHO0607BMVN-e-e.pdf

33. Farbwerke Hoechst A.-G., 1964, Dyeing of cellulosic materials, Farbwerke Hoechst A.-G publication.

34. Sika Australia Pty Ltd, 2003, MSDS: Sikafloor 261 Part B

35. IVL, Mikael Remberger Lennart Kaj Anna Palm John Sternbeck Eva Kvernes Eva Brorström-Lundén, 2003, Screening tertiary butylphenols, methylphenols, and long-chain alkylphenols in the Swedish environment, IVL Rapport/report B1594

36. US EPA, 1981, An exposure and risk assessment for phenol, EPA-440/4-85-013

37. Kirk-Othmer, Kirk-Othmer Encyclopedia of Chemical Technology Vol. 2 ALKYLPHENOLS, Copyright John Wiley & Sons, Inc
http://www.scribd.com/doc/30132752/Alkylphenols

38. HSDB database, Last Revision Date: 20091218, 2,4,6-Tris(1,1-dimethylethyl)phenol CASRN: 732-26-3, consulted 29/09/2010

39. HSDB database, Last Revision Date: 20091218, 2,4,6-Tris(1,1-dimethylethyl)phenol CASRN: 732-26-3, consulted 29/09/2010

40. Chen Guang, 2010, Clean gasoline and clean diesel fuel, Faming Zhuanli Shenqing publications, 7pp

41. HSDB database, Last Revision Date: 20091218, 2,4,6-Tris(1,1-dimethylethyl)phenol CASRN: 732-26-3, consulted 29/09/2010

42. Nistratov A.V, Reva S.V, Lukaski V.A, Novakov I.A, Frolova V.I, Lymareva P.N, Titova E.N, Lesnichuk A.V, 2010, Method and compositions for producing polymeric multilayer coating or flooring or pavement on sports grounds, GOU VPO Volgogradskii GTU, Russia, Russ. Publications, 11pp, STN datbase

43. Wang Cunqi, 2009, high-strength FPPE non-excavation sewage pipe made of modified polypropylene composition, Fujian Henggjie Plastic industry New Material Co, ltd. China, Faming Zhuanli shenqing Gongkai Shuomingshu publication, 8pp, STN datbase

44. Salavatova R.m, Niyazov N.A, 2007, Stabilizing agent for diene rubber compositions, OAO "Sterlitamakskii Neftekhimicheskii Zavod", Russia, Russ. publication, 8pp, STN datbase

45. Gotlib E:M, Grinberg L.P, Liakumovich A.G, Zharikov L.K, Kavun S.M, Logutov I.Yu, Khismatullin, S.G, 2002, Production of stabilizers for vulcanized rubber, Opytno-Promyshlennoe Predpriyatie Tsentra Po Razrabotke Elastomerov, Russia, Russ. Publications, STN datbase

46. Cherenyuk IP, Levechenko SI, 1986, Unsaturated rubber stock, Otkrytiya, Izobret, 1986, (25), p95, STN datbase

47. Kinch David Alan, Garner Robert, 1972, Rodenticidal 2,4,6 trialkylphenols, Imperial Chemical Industries Ltd. , STN datbase

48. Zaitsev N.F, Davletshin R.H, Arkhireev VP, Cherevin VF, Sadova AN, Tarasov NF, 2002, Ethylene-vinyl acetate copolymer-based adhesive compositions, Otkrytoe Aktsionernoe Obshchestov "Sevilen", Russia, Russ. Publications, STN datbase

49. Bityukov V:K, Tikhomirov S:G, Tarasevich T.V, Ososhnik I.A, Karmanova O.V, Korchagn V.I, Popova L.V, 2008, Modified vegetable oil production wastes used as processing aids in rubber composition, Obshchestvo s Organichennoi Otvetstvennost'yu " SOVETEKh", Russia, Russ. publications, 8pp, STN datbase

50. Tikhomicrov GS, Pryakhina EA, Krivosheitseva TS, Molodykha AV, 1986, Carboxylate latex for carpet-backing coatings, Kauchuk I Rezina (1986), (4), p9-10, ISSN 002-9466, STN datbase

51. Tokyo Ohka Kogyo Co. Ltd, Japan, 1983, Jet-recording inks, Jpn, KoKai Tokkyo Koho publications, 4pp, STN datbase

52. Hong L, Fidler E, Enick R, Marentis R, 2008, tri-tert-butyl phenol: a highly CO2-soluble sand binder, Journal of Supercrititcal Fluids, 44(1), p 1-7, ISSN 08968446, STN datbase

53. SSB, Bensinstatistikk 2009, http://www.ssb.no/emner/01/03/10/energiregn/tab-2010-04-23-01.html

54. Private communication with ATC, november 2010

55. SSB, Energiregnskap 2009 (foreløpige tall, retrieved 07.12.10),
http://www.ssb.no/emner/01/03/10/energiregn/

56. SSB, Energiregnskap 2009 (foreløpige tall, retrieved 07.12.10),
http://www.ssb.no/emner/01/03/10/energiregn/

57. Environment agency (UK), 2007, Environmental risk evaluation report: para-C12-alkylphenols(dodecylphenol and tetrapropenylphenol, Environment agency publication, ISBN: 978-1-84432-789-8
http://publications.environment-agency.gov.uk/pdf/SCHO0607BMVN-e-e.pdf

58. SSB, Statistikk 2009 for lubricants,
http://statbank.ssb.no/statistikkbanken/

59. Plenco, plastic engineering company,
http://plenco.com/phenolic-novolac-resol-resins.htm

60. Private communication with ERMA, December 2010
www.erma.org.uk

61. SSB, Statistics 2009, Pneumatic tyres
http://statbank.ssb.no/statistikkbanken/

62. European tyre recycling association (ETRA) website, Introduction to tyre recycling, consulted November 2010
http://www.etra-eu.org/ac121.htm

63. Environment agency (UK), 2007, Environmental risk evaluation report: para-C12-alkylphenols(dodecylphenol and tetrapropenylphenol, Environment agency publication, ISBN: 978-1-84432-789-8
http://publications.environment-agency.gov.uk/pdf/SCHO0607BMVN-e-e.pdf

64. Environment agency (UK), 2007, Environmental risk evaluation report: para-C12-alkylphenols(dodecylphenol and tetrapropenylphenol, Environment agency publication, ISBN: 978-1-84432-789-8
http://publications.environment-agency.gov.uk/pdf/SCHO0607BMVN-e-e.pdf

65. HSDB database, last updated 03/05/2003, Dodecyl-phenol, consulted in November 2010
http://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+386

66. HSDB database, last updated 2009-12-18, 2,4,6-Tris(1,1-dimethylethyl)phenol, consulted in November 2010
http://toxnet.nlm.nih.gov/cgi-bin/sis/search

67. Environment Canada, 2009, Screening Assessment for the Challenge: Phenol, 2,4,6-tris(1,1-dimethylethyl)- (2,4,6-tri-tert-butylphenol) (CAS 732-26-3)
http://www.ec.gc.ca/substances/ese/eng/challenge/batch2/batch2_732-26-3_en.pdf

68. Environment agency (UK), 2007, Environmental risk evaluation report: para-C12-alkylphenols(dodecylphenol and tetrapropenylphenol), Environment agency publication, ISBN: 978-1-84432-789-8
http://publications.environment-agency.gov.uk/pdf/SCHO0607BMVN-e-e.pdf

69. IVL, Mikael Remberger Lennart Kaj Anna Palm John Sternbeck Eva Kvernes Eva Brorström-Lundén, 2003, Screening tertiary butylphenols, methylphenols, and long-chain alkylphenols in the
Swedish environment, IVL Rapport/report B1594

70. Environment Canada – Health Canada, 2008, Screening assessment of the challenge: phenol 2,4,6-tris(1,1-dimethylethyl) – (2,4,6-tri-tert-butylphenol), CAS 732-26-3
http://www.ec.gc.ca/Publications/default.asp?lang=En

71. US EPA, 1981, An exposure and risk assessment for phenol, EPA-440/4-85-013

72. Nordic Council of Ministers, 2008, TemaNord 2008:530: Screening of phenolic substances in the Nordic environments, Nordic Council of Ministers publication, ISBN 978-92-893-1681-1

73. SSB, Holmengen N., 2009, Use and emissions of hazardous substances in Norway, 2002-2007,SSB publication, ISBN 978-82-537-7688-0

74. Environment Canada, 2009, Screening Assessment for the Challenge: Phenol, 2,4,6-tris(1,1-dimethylethyl)- (2,4,6-tri-tert-butylphenol) (CAS 732-26-3)
http://www.ec.gc.ca/substances/ese/eng/challenge/batch2/batch2_732-26-3_en.pdf

75. http://www.miljostatus.no/Tema/Avfall/Farlig-avfall/Spillolje/

76. Environment Canada, 2009, Screening Assessment for the Challenge: Phenol, 2,4,6-tris(1,1-dimethylethyl)- (2,4,6-tri-tert-butylphenol) (CAS 732-26-3)
http://www.ec.gc.ca/substances/ese/eng/challenge/batch2/batch2_732-26-3_en.pdf

77. Environment agency (UK), 2007, Environmental risk evaluation report: para-C12-alkylphenols(dodecylphenol and tetrapropenylphenol, Environment agency publication, ISBN: 978-1-84432-789-8
http://publications.environment-agency.gov.uk/pdf/SCHO0607BMVN-e-e.pdf

78. Environment agency (UK), 2007, Environmental risk evaluation report: para-C12-alkylphenols(dodecylphenol and tetrapropenylphenol, Environment agency publication, ISBN: 978-1-84432-789-8
http://publications.environment-agency.gov.uk/pdf/SCHO0607BMVN-e-e.pdf

79. Dekkretur website, Statictics, Consulted November 2010
http://www.dekkretur.no/statistikk.html

80. Environment agency (UK), 2007, Environmental risk evaluation report: para-C12-alkylphenols(dodecylphenol and tetrapropenylphenol, Environment agency publication, ISBN: 978-1-84432-789-8
http://publications.environment-agency.gov.uk/pdf/SCHO0607BMVN-e-e.pdf

81. Ragnsells website, consulted in November 2010
http://www.ragnsells.no/defaultnobox.aspx?pageId=56

82. Dekkretur website, Statictics, Consulted November 2010
http://www.dekkretur.no/statistikk.html

83. Environment agency (UK), 2007, Environmental risk evaluation report: para-C12-alkylphenols(dodecylphenol and tetrapropenylphenol, Environment agency publication, ISBN: 978-1-84432-789-8
http://publications.environment-agency.gov.uk/pdf/SCHO0607BMVN-e-e.pdf

84. SSB, Holmengen N., 2009, Use and emissions of hazardous substances in Norway, 2002-2007,SSB publication, ISBN 978-82-537-7688-0

85. Nordic Council of Ministers, 2008, TemaNord 2008:530: Screening of phenolic substances in the Nordic environments, Nordic Council of Ministers publication, ISBN 978-92-893-1681-1

86. Nordic Council of Ministers, 2008, TemaNord 2008:530: Screening of phenolic substances in the Nordic environments, Nordic Council of Ministers publication, ISBN 978-92-893-1681-1


BERGFALD
miljørådgivere