WHITE PAPER

Lubrisense™ 201314

POLYUREA GREASES

Dr. Carl Kernizan
Axel Americas LLC

Application case studies

John Lorimor
Axel Americas LLC

AXEL
AXEL CHRISTIERNSSON

POLY = MANY
EDITORIAL, "POLYUREA FOR DUMMIES".

Polyurea greases are becoming an interesting alternative to more conventional soap-based products as demands increase to be able to tailor different physical and chemical properties towards specific applications. In itself, the word polyurea is derived from two Greek words, πολυ – poly, meaning "many"; and ουρίας – oûron, meaning "to urinate" (the latter term referring to the substance urea found in urine, rather than urine itself). The implication of "poly = many" is that there is obviously not just one type of possible polyurea grease but a whole cavalcade of molecular combinations, all with different structures and properties. According to an anonymous source within the lubricants industry, *"polyureas are like women; there are many and they are all beautiful"*. A veritable dream for any creative grease formulator? In "simplistic" terms, according to Wikipedia, polyurea is a "type of elastomer that is derived from the reaction product of an isocyanate component and a synthetic resin blend component through step growth polymerisation. The isocyanate can be aromatic or aliphatic in nature. It can be monomer, polymer, or any variant reaction of isocyanates. The resin blend may be made up of amine-terminated polymer resins, and/or amine-terminated chain extenders". Or, in even more casual terms:

isocyanate + amine = polyurea

Polyurea greases are almost always chosen because of their high temperature properties. Art Polishuk, in his tome, A Brief History of Lubricating Greases, claims that "one of the unique properties of polyurea greases is that they tend to thicken with an increase in temperature. This may contribute to their long performance in bearings at elevated temperatures. Their long bearing life may also be due to the fact that they contain no metals to catalyse oxidation". Another reason for the choice of a polyurea grease may be for specific rheological properties where some versions exhibit extreme thixotropic behaviour and can be made mechanically instable by design. Polyurea greases represent some 4% of the total worldwide grease production. They are most popular in Japan whereas, in other areas, they have not caught on significantly, most probably due to the health and safety issues concerning the handling of the raw materials.

POLYUREA GREASES, AN OVERVIEW

by Dr. Carl Kernizan, Axel Americas LLC

DR. CARL KERNIZAN, is today the Vice President of Business Development & Corporate Strategy at Axel Americas LLC, specializing in technical and business strategies to meet the existing and future market demands in the entire Americas. He has previously worked as Technical Director of Jesco Resources Inc. (assets acquired by AXEL in 2011), as both Product Manager and Research Chemist in the lubricant additives business, and as Principal Research Tribologist in the rolling bearing industry. Carl holds a B.S. in Chemistry and a Ph.D. in Physical Chemistry from the City University of New York and has conducted post-doctoral research at Kansas State University. He has authored over 30 publications including 2 patents and received NLGI's Clarence E. Earle Award in 1998 and the NLGI Fellow's Award in 2002.

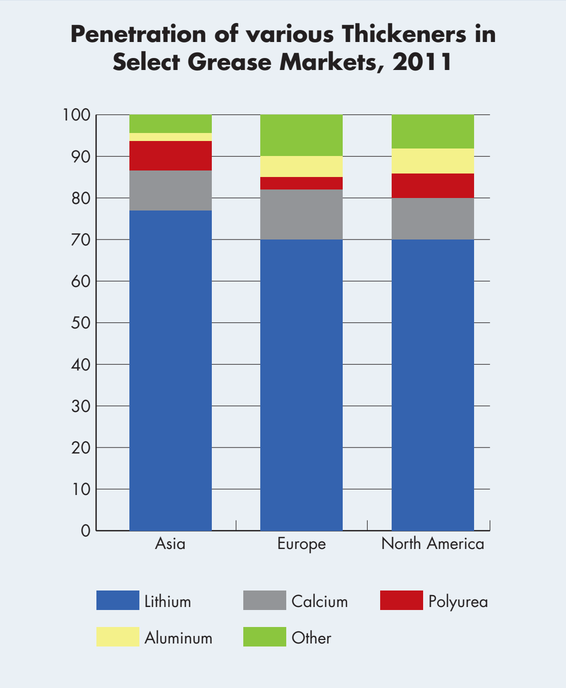
JOHN J. LORIMOR, is currently Global Technical Director for the AXEL Group with the primary responsibility for the strategic management of AXEL's worldwide technical resources. Over the past 20 years, John has held a variety of leadership roles at some of the most well-known names in the grease and additives industry. He received his bachelor degree in Chemical Science from Kansas State University in 1994, and MBA from the University of Phoenix in 2001. He has authored numerous papers on grease related topics, and was recognized with the NLGI Author Award at its 2010 annual meeting. John is an STLE Certified Lubrication Specialist (C.L.S.®), and was among the first recognized by NLGI as a Certified Lubricating Grease Specialist (CLGS®).

Introduction

The invention and development of polyurea thickened greases is one the most important advances in grease technology since the end of the Second World War. The technology was developed in Japan where it is still an impressive 21% of their grease market. These ashless non-soap greases are generated by the step-growth polymerisation reaction of different isocyanates and amines in various mineral or synthetic base oils. These polyurea thickened greases tend to have high temperature performance, inherent anti oxidative properties and can exhibit either high shear stability or thixotropic behaviours. These properties have recently made them the preferred choice for filled-for-life applications in both bearings and constant velocity joints and have increased their importance in steel plants and electric motors. However, their positioning as multipurpose greases has been limited by the high safety required with the storage and handling of their toxic raw materials and difficulty in their manufacture and packaging. Unlike Japan, the last three industry surveys place them at under 5% of the grease market which classifies them as specialty greases.

Chemistry

Ureas or carbamides are organic compounds with the chemical formula **$CO—(NH_2)_2$**. The molecule has a central carbonyl (**$C=O$**) joined by two amine (**NH_2**) functional groups. These compounds are synthesised in the body of many organisms as part of the urea cycle, either from the oxidation of amino acids or from ammonia. They are also commonly used in fertiliser, agriculture, coatings, plastics and the pharmaceutical industry. Commercial production



POLYUREA MARKET SHARE
(SOURCE: GREASE WEBINAR, KLINE & CO, 2011)

of ureas is on the order of 100,000,000 tons per year worldwide. They were first discovered in urine in 1727 by the Dutch scientist Herman Boerhaave and were the first organic compound artificially synthesised, without the involvement of living organisms, by the reaction of inorganic starting materials, by the German chemist Friedrich Wöhler in 1828.

The term urea also refers to a class of chemical compounds that are derived from the reaction product of mono or diisocyanates and combinations of aliphatic, alicyclic, or aromatic amines through step-growth polymerisation. This reaction is a type of polymerisation mechanism in which bi-functional or multifunctional monomers react to form first dimers, then trimers, longer oligomers and eventually long chain polymers that are called polyureas.

The isocyanates and amines have the general chemical formulations, **O=C=N—R—N=C=O** and **H_2N—R'—NH_2**, respectively. The connecting **R** and **R'** chains in either compounds, preferably

APPLICATION CASE STUDIES

by John Lorimor, Axel Americas LLC

AGRICULTURAL EQUIPMENT

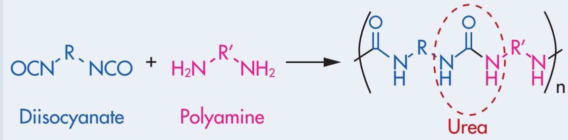
The agricultural industry is tough on equipment, just ask John Deere. Working in harsh environments and heavy crops, Deere knows down equipment is not an option. Before John Deere puts their reputation on the line with branded grease, it is put through grueling tests to make sure it can combat its toughest enemies, like extreme pressures, severe temperatures, and water – better than other greases. Engineers at John Deere have developed some of the most stringent grease performance standards in order to prevent downtime and extend the life of its customers' equipment. These standards call for greases that can perform in the myriad of hostile conditions their customers face every day, including hot or cold climates, wet and/or dirty environments, and even protect in the event of infrequent relubrication. Based upon many years of field-proven, hands on experience, for the most severe conditions of agricultural service John Deere recommends polyurea thickened greases. MP SD Polyurea grease is John Deere's best multi-purpose product, and is ideal for providing top-notch protection in hostile environments.

range from 2 to 20 carbon atoms groups and can be straight or branched chained saturated, unsaturated or aromatic groups. However, in the modern grease industry, the selection is generally limited to three diisocyanates and a series of amines. The three diisocyanates are Methylene diphenyl diisocyanate (MDI), hexamethylene diisocyanate (HDI) and Toluene diisocyanate (TDI). The amines include monoamines such as aniline, dodecylamine, hexadecylamine, octadecylamine, toluidene, tertiary butyl aniline and fatty amines such as laurylamine, palmitylamine and oleylamine. They also include diamines such as ethylenediamine, dodecanediamine, cyclohexanediamine and phenylenediamine.

Isocyanate and an Amine-terminated (–NH_2) resinblend

2 MA + 2 DI + DA ——————> MA – (DI – DA – DI)$_n$ MA

MA = Monoamine, DI = Diisocyanate, DA = Diamine and n>2.

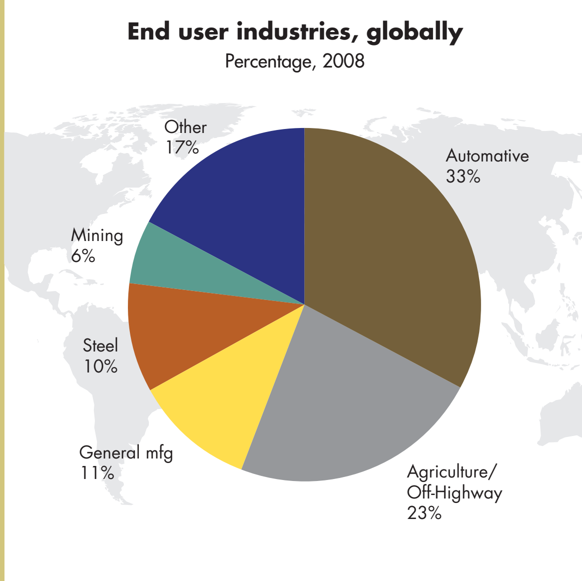


POLYUREA REACTION

The general reaction for forming mono, di, and tetraureas can be illustrated by the following:

2 MA + 2 DI + DA ——————> MA – (DI – DA – DI)$_n$ MA

MA = Monoamine, DI = Diisocyanate, DA = Diamine and n>2.



The polyurea thickener has proven itself extremely robust and versatile, providing diverse applications on expensive agricultural equipment outstanding long-term protection from rust corrosion, wear on moving parts, all the while remaining easy to dispense from onboard lubrication systems. Polyurea greases last longer than other greases, the ashless thickener proven to be outstanding in resisting thermal oxidation. John Deere is so confident in the long term life of polyurea grease that it uses the thickener technology extensively in difficult factory fill grease

END USER SEGMENTATION

OVERVIEW OF AXEL AMERICAS PRODUCTION FACILITY IN ROSEDALE MISSISSIPPI

applications, such as on the inside bearing of the torque sensing unit on a John Deere combine. Other common grease applications on agricultural equipment include heavily loaded ball and roller bearings, steering racks, U-joints, ball & socket or other articulation joints, pin & bushings and other accessory attachment configurations that require heavy-duty protection. Agricultural harvesting equipment such as John Deere combines are multi-functional, and can be adapted to process row planted crops by the addition of a row unit. In the case of harvesting corn, this row unit is called a corn head. These accessory units contain many moving parts driven by a slow speed gear case in order to deconstruct the stalk and remove the crop. Corn head grease is a polyurea thickened, soft NLGI 0 grade lubricating grease. A hybrid between a fluid gear lubricant and lubricating grease, it functions as a robust gear lubricant when meshed in the interface between two gear sets, such as those in a John Deere combine corn head gear case. However, because it is grease rather than a fluid gear lubricant, it stays in the gear case even when a worn seal would cause a traditional fluid lubricant to leak. This grease property is described as being thixotropic, meaning the grease softens and flows when sheared, then thickens back to its normal consistency to provide a leak proof sealing barrier when the equipment is not running. Corn head grease contains all the necessary additives to resist wear and corrosion, in addition other ingredients assure that corn head grease will not wash away if

CORNHEAD (SOURCE: WWW.DEERE.COM)

Polyureas can also be formed by the reaction of isocyanates and water to form a carbamic acid intermediate. This acid quickly decomposes by splitting off carbon dioxide and leaving behind a complex amine. This amine then reacts with another isocyanate group to form the polyurea linkage. This two- step reaction is used in what is commonly called polyurea/urethane foam formation.

The reactivity of isocyanates makes them harmful to living tissue. They are toxic and are known to cause asthma in humans, both through inhalation exposure and dermal contact. Precaution should always be taken when handling them. Exposure to diisocyanates can cause different medical conditions. Most common are respiratory problems such as a runny nose, coughing or nose bleed. In the case of the amines, it is difficult to be specific since there are many different types involved. Many of them are, however, quite nasty materials. Aromatic and structurally similar amines comprise one of the major groups of carcinogens known to man. It is therefore of the utmost importance to avoid contact with these materials and great detail should be given to health and safety issues when handling these raw materials. However, in paradox, once they have been fully reacted into finished polyurea compounds, they are no longer harmful or toxic. In fact, some polyurea greases are even approved for use in foodgrade applications where there is risk for incidental contact.

Grease Manufacturing

Commercial production of polyurea thickened greases usually follows a three step manufacturing process. In the first step, approximately 9 to 20 weight per cent of the selected isocyanates and amines together with about 40 weight per cent of base oils are introduced in a suitable reaction kettle. The reactants can be added either all at once or sequentially for single or double kettle thickener processes, respectively. Once the blend is in the reaction kettle, it is slowly mixed from temperatures ranging from 21°C to 204°C (70°F to 400°F) for

a period sufficient to cause formation of the thickener. Although, the reaction is exothermic, external heating is required to ensure completion and generation of a stable thickener complex. The NLGI grade of the thickener is pre-determined by the amount of base oil introduced at the start of the process.

In the second step, suitable liquids and solid additives are added to the hot thickener in the same kettle or to a second or finishing kettle. Portions of the remaining base oils are added to the thickener to achieve the desired viscosity grade and cool it to temperatures suitable for the addition of other performance additives. These additives include anti-oxidants, extreme pressure, anti-wear agents and dyes.

In the final step, the fully additivated grease is homogenized to achieve the desired NLGI grade. Homogenisers are preferred over colloid mills since they generate polyurea greases with better texture and can significantly adjust the NLGI grade of the grease. Depending on the starting material and the plant equipment, the finished grease may require additional cooling prior to packaging in a suitable container.

Recently, polyurea grease manufacture has been simplified by the use of commercially available polyurea powders. These powders are generated by solvent extraction of the base oil from the polyurea thickener manufactured by the previously explained first step of the manufacturing process. The grease is then manufactured by solubilizing the powder at the desired concentration in base oils at medium temperatures with continuous mixing. Once formed, additional oil and performance additives are added to the thickener to achieve the desired performance requirements. This approach significantly eliminates the risks involved in handling the toxic raw materials but limits the types of polyurea greases that can be generated since this option is controlled by the composition of the powder.

unwanted water is present either as spray or contaminant. Because Corn Head Grease is thixotropic, oxidation resistant, and fully fortified with the proper additives it is the best possible grease for use in corn head gear cases and it also performs well in irrigation system gear cases, golf and turf cutting gear cases, and other gear cases requiring an NLGI 0 grade grease.

SEALED FOR LIFE BEARINGS

Electric motor and automotive wheel bearings are two demanding sealed for life applications where polyurea greases thrive. Operating temperatures in these applications can frequently reach 150-180°C, significantly stressing conventional grease thickeners. The dropping point test gives an indication of the temperature at which the grease will melt or the oil will separate from the thickener. Due to the high temperatures that can be reached in these bearing applications, grease with a high dropping point is extremely desirable. Polyurea-thickened greases have dropping points of 260°C or higher. One of the most common grease degradation mechanisms is oxidation. Conventional grease thickeners are based upon the metal salt of fatty acids. Metals can have a catalytic effect on oxidation, speeding up grease degradation reactions. Selection of a thickener system which is not formed from metallic components significantly reduces this limiting factor in grease life. Polyurea based greases are completely metal-free, and as such have outstanding resistance to oxidation.

High Temperature Grease Life test results give a good indication of a greases ability to operate under extreme conditions. In this type of testing, polyurea greases can offer

THROUGH OUR CUSTOMISED LABEL™ STRATEGY, WE BECOME A CHAMPION OF YOUR BRAND, MANUFACTURING GREAT QUALITY INDUSTRIAL LUBRICATING GREASES TIME AND TIME AGAIN, IN YOUR NAME, ON YOUR BEHALF, CUSTOMISED TO MEET THE NEEDS OF YOUR CUSTOMERS.

operational lifetimes of up to 50% longer than conventional complex thickeners. This long grease life can extend the life of bearings running at high speeds and high temperatures.

CONSTANT VELOCITY JOINTS (CVJ)

A CVJ is a torque transmitting coupling in which the input and output shafts have the same velocity. They are used in vehicle drivelines to smoothly transmit the energy from the gearbox output shaft to the wheels. In today's modern car or light truck, the biggest volume of grease is used to lubricate CVJs, and these greases are expected to last for the lifetime of the vehicle.

Polyurea thickened CVJ greases were first introduced in 1978, and due primarily to progressively increasing temperature requirements have grown to become the dominant thickener for this application. CVJs are complex systems that are tribologically very highly stressed. In the most demanding cases, plunging ball joint temperatures can reach 150–180°C. Under these severe temperature conditions, the high dropping point and oxidative resistance of the polyurea thickener system allow it to survive. One primary advantage of urea thickeners is that the building blocks can be adjusted to modify the performance of the finished grease. One finished grease property that can be imparted is thixotropy. Thixotropy is a shear thinning rheological behavior of certain urea derivatives, and in the case of the CVJ application is very beneficial in contributing to reduced lubricant starvation.

STEEL MILL CONTINUOUS CASTORS

In continuous casting (CC), molten steel is refined by blast furnace processing and then solidified into an intermediate

Polyurea complex greases are produced when calcium based soaps or complexing agents are added to the formed thickener. In addition to the excellent properties of normal polyurea grease, these agents add inherent water resistance, extreme pressure and wear protection properties that increase the multipurpose capabilities of these polyurea complex greases.

Application & Properties

Diurea greases are the most widely used polyureas in the current grease market. They can be manufactured either with TDI or MDI isocyanates and are often designated by the specific starting materials. The TDI alkyl aryl polyurea can have dropping points as high as 250°C (482°F), excellent water resistance, low oil separation, uncanny thixotropic behaviour and superior mobility and pumpability. These performance parameters allow them to perform exceptionally well in filled for life ball bearings found in boat trailers, fans, high speed spindles and alternator bearings, respectively. Their thixotropic behaviour, pumpability and mobility also allow them to be used in agricultural, construction and forestry equipment fitted with automated lubrication dispensing units optimized for multiple contact zones and lubrication points. MDI polyurea greases tend to have excellent work stability and, when additivated with the suitable antioxidants, have replaced TDI greases in constant velocity joints, generator and electric motor bearings. Their superior water resistance has also made them suitable for use in continuous casting segments of steel mills. Tetraurea greases can also be used in electric motor bearings but their selection is less desirable since they tend to harden when exposed to high temperatures or stored over time. Although polyurea thickened greases are widely used in modern lubrication applications, special consideration should be taken with their selection since they tend to have low levels of compatibility with other types of greases including other polyureas.

product called the slab, billet or bloom. This intermediate steel product is then supplied to the rolling mills for finishing. The bearings which support the moving slab combine high loads and elevated temperatures with low rotational speed. This presents difficulties in creating a lubricant film between the bearing's rollers and raceways. High viscosity base oil greases must be selected to resist corrosion and aid in sealing as a result of continuous exposure to secondary cooling water spray and hard debris contamination.

Polyurea greases have many desirable properties which have made them successful in CC applications. For continuous casters, the most widely used lubrication method is the centralized grease distribution system. These systems pump a relatively small amount of grease at frequent intervals to the bearing. This frequent cycle keeps the bearing full with fresh grease while also purging old grease and contaminants. Good flow properties are essential for grease to be used in steel plant applications and polyurea grease possess excellent pumpability characteristics, particularly at low shear rate. The thixotropic nature of urea based greases provides an excellent sealing barrier to prevent water and abrasive foreign particles from entering the bearings. In addition, the high dropping point (>260°C) and excellent oxidative stability offered by urea thickened greases provide extended high temperature capability, greatly enhancing high temperature bearing life.

HIGH TEMPERATURE APPLICATION; CONTINUOUS CASTING

NEXT ISSUE

The next issue of the Lubrisense™ White Papers will focus on lubricants for heavily loaded applications, especially greases for open gears. Traditionally, such products have contained substantial amounts of solid particles such as graphite and/or molybdenum disulphide. However, in recent years, doubts have been raised concerning the need for or even the suitability of using such materials in this type of product. We are pleased that Johann-Paul Stemplinger from the Gear Research Centre FZG in Munich Germany has agreed to be our guest author and will describe wear behavior in grease lubricated gears. In addition, we will present case studies where greases containing no solids have outperformed conventional types of graphited products.

As usual, we encourage reader contribution, feedback and proposals concerning relevant topics for future issues of our White Papers.

Editor Graham Gow / graham.gow@axelch.com

AXEL CHRISTIERNSSON AB
P.O. BOX 2100
SE 449 11 NOL
SWEDEN
TEL +46 (0) 303 33 25 00
FAX +46 (0) 303 33 25 90

AXEL CHRISTIERNSSON BV
1 FEBRUARIWEG 13
4794 SM HEIJNINGEN
THE NETHERLANDS
TEL +31 (0) 167 52 29 80
FAX +31 (0) 167 52 22 71

AXEL FRANCE SAS
46 RUE DE GOISE, BP 8821
FR-79028 NIORT CEDEX 9
FRANCE
TEL +33 (0) 49 77 13 71
FAX +33 (0) 5 49 73 95 30

AXEL AMERICAS LLC
1440 ERIE
N, KANSAS CITY, MO 64116
PO. BOX 12337
USA
TEL +1 (0) 816 471 4590
FAX +1 (0) 816 471 2240

WWW.AXELCH.COM
INFO@AXELCH.COM

A COMPANY IN THE FAIRFORD GROUP