WHITE PAPER

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REACH
an EU regulatory framework for chemicals

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Additives in grease formulations

AXEL
AXEL CHRISTIERNSSON

Legislation – REACH

EXISTING CHEMICALS REGULATIONS

The current legal arrangements for chemical regulation in the EU have evolved over a 30-year time frame and they naturally have a form and complexity reflecting this development. In essence they operate broadly by distinguishing between existing and new substances with most of the burden of regulatory obligations falling on new substances.

REACH – WHAT IS IT?

The development of REACH proposal dates back to the mid-1990s and the intent to improve and modernise how chemicals are regulated in the EU

The result of this the White Paper[1] – '*Strategy for a future Chemicals Policy*', published in February 2001.

Emerging out of the White Paper, on 29 October 2003, the European Commission adopted Proposals for a new EU regulatory framework for chemicals known as REACH[2] (Registration, Evaluation and Authorisation of Chemicals) with the political objectives to promote a high level of protection of human health and the environment whilst maintaining and enhancing the competitiveness and innovative capability of all parts of the chemical supply chain.

REACH sets out proposals for learning more about all manufactured and imported chemicals, it introduces a precautionary approach on controlling chemicals of high concern and reverses the burden of proof to industry to ensure all parts of the supply and use chain play their part in determining and then managing any identified risks.

This paper summarises the main characteristics of REACH – as set out in the revised Commission proposal – and it is important to note that the exact scope and detail of REACH will change during the process of political adoption. The paper briefly explores the impact on a typical grease supply chain and identifies the preparatory actions ahead of REACH adoption.

REACH – THE PROPOSALS

The REACH proposals have three main phases: **Registration, Evaluation** and **Authorisation/ Restriction**. REACH is a series of actions based on drawing together information, generating a hazard assessment and gathering exposure and use details in order to carry out a risk assessment and to then identify risk management recommendations.

This process is shown very simply in Figure 1.

REGISTRATION

The new proposals have Registration as the centrepiece. This basic obligation will require companies (or more accurately legal entities) manufacturing or importing chemicals 'as is' or in preparations above a 1 tonne threshold per year, to register, gather information and data and, based on information from downstream users, identify

ADDITIVES

Almost all modern oils and greases contain additives to enhance various aspects of lubricant performance. One of the advantages of grease compared to a fluid oil is that its solid gelled structure allows a certain flexibility in the selection of additives. Solubility and insolubility are key factors in this selection. In lubricating oil formulations, additives must be soluble or very highly dispersed in the liquid to avoid phase separation or sedimentation. In contrast, solubility is not necessarily a pre-requisite in grease formulations. The gelled structure is capable of retaining both soluble and insoluble additive components within its solid matrix.

On the other hand, since the great majority of additives are designed for optimum performance in liquid lubricants such as motor oils and hydraulic fluids, they are often highly polar substances and can therefore interfere with the thickening mechanisms within a grease. This interference inadvertently leads to a breakdown in structure and catastrophic degelling as a result. So it is very important indeed to select the right chemistry for a grease additive.

Some additives are required to be available at the machinery surface, whereas others perform their duty best by being dispersed thoroughly in the base oil or even the thickener system.

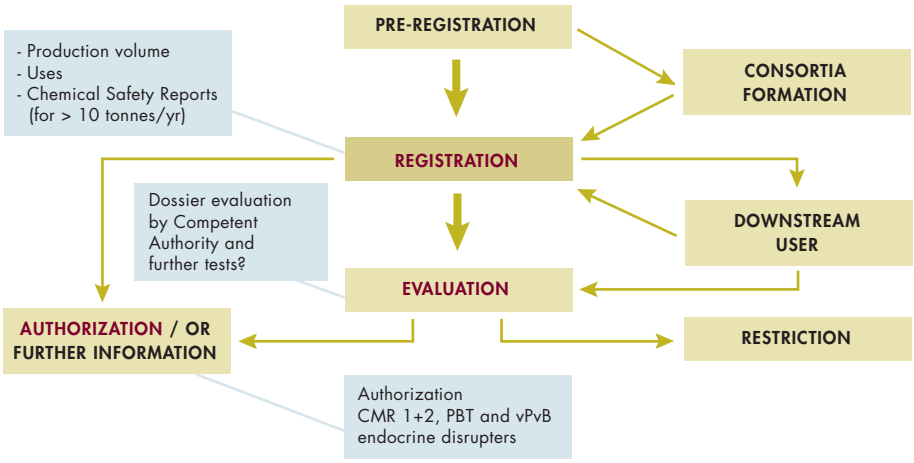


FIG. 1
SIMPLIFIED REACH PROCESS

intended end uses and exposure and then finally to assess risk and communicate risk management arrangements to all downstream users and to a central agency.

REACH mandates information mainly based on volume, it requires gathering and submission of information in a technical dossier and for higher volume substances a chemical safety assessment and report. It will also require information on risk management, exposure scenarios and acceptable intended uses to be communicated through supply chains. It is aimed not just at manufacturers and importers of all chemicals but will draw in downstream users as well since their role is to communicate back up the supply chain information on exposure and intended use.

The design, scope and obligations of registration are complex and further detail can be found in the Commission REACH proposal[2] and the Commission's Guidance on REACH[3]. There are some important exemptions to REACH especially the exclusions for substances of low concern in Annexes II and III and – at least for the foreseeable future – polymers.

There will be a pre-registration phase which will allow consortia building and identification of available data. The deadlines for Registration vary, with the first phase on higher volume chemicals and carcinogens, mutagens and reprotoxins (CMRs). The timings for the proposed registration actions are presently set at:

By **Year 3** following implementation for high production volume (HPV) chemicals (1,000 tonnes or more per year per manufacturer or importer) and CMRs in volumes of 1 tonne or more;
By **Year 6** for production volumes in the range of 100 - 1,000 tonnes;
By **Year 11** for low production volume chemicals (1 - 100 tonnes).

Until recently, most additives and additive packages were developed by suppliers with the large volume lubricating oil market in mind. Over the past few years, however, this has been changing.

In a soap thickened grease, additives which need to be present at the metal surface have to be able to compete with the polar molecules of the thickener system. The soap itself may well have already fully coated the metal surface leaving nothing for the additives to react with. A traditional oil soluble additive, developed specifically for fluid oils, could therefore exhibit inferior performance in a grease if it was actually required to be available at the metal surface.

The correct selection of functional additives is clearly very significant in enhancing grease performance.

ANTIOXIDANTS

Degradation of both the base fluid and the thickener can be prevented, or at least delayed, by the use of an effective antioxidant system. Antioxidant solubility in the different specific grease components can greatly enhance their individual functionality. The most common antioxidants are phenol and/or amine derivatives, although sulphur and phosphorus containing compounds have also been used.

FIG. 2 COSTS AND TIMEFRAME FOR REGISTRATION

TONNES / YEAR	1-10	10-100	100-1,000	>1,000
COST, 000'S EUROS	20	100-240	250-400	400-1000
REGISTRATION TIME AFTER ADOPTION	11 YEARS	11 YEARS	6 YEARS	3 YEARS
CMR 1 & 2	3 YEARS	3 YEARS	3 YEARS	3 YEARS

Registration will require – for substances above the 10 tonne per annum category – the development of a chemical safety assessment, the submission of this risk assessment in the form of a chemical safety report to the Central Agency and key information on risk management measures down the supply chain to users.

The financial implications of REACH have been well debated and there is a huge range of estimates for the costs of REACH, especially the costs associated with gathering the information/data for a substance against the data requirements specified for each volume threshold. A worst case scenario is shown in figure 2 assuming no existing data. However, most substances have some information, particularly the high volume chemicals and there is recognition that alternative approaches using categories, surrogate data and read-across approaches may limit the extent of new testing. This question of ensuring risk is assessed and necessary forms of risk management communicated downstream is a radical part of REACH. Users of chemicals will have an important part to play in supporting this assessment of risk with the duty to ensure information on exposure and use flow back up the supply chain. Downstream users will have to verify their use is supported and assessed for risk.

EVALUATION

The REACH proposals outline different activities during the evaluation phase. Evaluation is effectively the part of the REACH process where the regulators either in the ECA or at the National Government level begin to intervene in the process.

The first part is a compliance check of the submitted registration which is done to verify and assess completeness rather than the quality of the content of the technical dossier. The next stage begins with the process of technical dossier evaluation which represents a quality assessment of selected elements of the registration together with a mandatory evaluation of any testing proposals made for substances registered at levels greater than 100 tonnes per annum. This mandatory assessment of testing proposals is designed to ensure that animal testing is maintained to a minimum. The next phase is substance evaluation. This is the process where criteria are established for prioritising substances for further review.

AUTHORISATION AND RESTRICTION

The substances selected for the authorisation system will be those identified and confirmed to have any of the following properties:

CORROSION INHIBITORS AND PASSIVATORS

These additives obviously need to be available and active at the metal surface. Rust inhibitors are used to prevent corrosion on ferrous metals and chemical attack in general. Very careful selection is required, taking into account the particular metals needing protection and the specific corrosion threat to be thwarted. At temperatures above 150°C, certain types of rust inhibitors can degrade rapidly and very special chemistries are therefore needed for high temperature greases.

Copper and its alloys are sensitive to chemical attack and can even act as catalysts for the oxidation of organic compounds. Different types of passivators are therefore used in many grease formulations, often with a dual purpose, both to protect the yellow metal surfaces from tarnishing and to inhibit the base oil and thickener against catalytic degradation effects.

ACTIVATORS

Additives are also used to activate or promote desirable reactions in the manufacturing process and to stabilise the gel structure of especially clay, silica gel and even conventional calcium greases. Typical compounds include alcohols, polyglycols, acetone, propylene carbonate and simply water.

EXTREME PRESSURE ADDITIVES

With the right thickener and base oil combination, the

- Carcinogens, Mutagens and Reprotoxins (Categories 1 and 2) (CMR)
- Persistent, Bioaccumulative and Toxic substances (PBT)
- Very Persistent and very Bioaccumulative substances (vPvB)
- Other substances with serious and irreversible effects of an equivalent level of concern.

For the authorisation of these substances and their continued use, it will be necessary to demonstrate that the risk from use is adequately controlled or that the socio-economic benefits outweigh the risks.

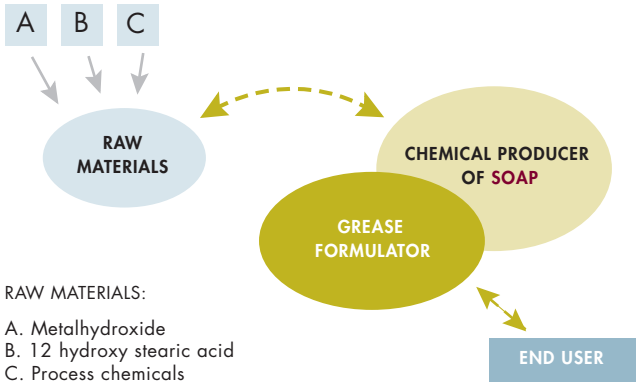
SIMPLE GREASE FORMULATION

In order to detail the likely processes and information that is necessary to be gathered an example of a simple grease formulation is taken through the REACH proposals.

SOAP THICKENER – INFORMATION FLOW

The soap thickener is a critical part of the grease formulation. At the beginning of the supply chain, all of the raw materials used directly in the manufacture of the soap, i.e. the Lithium Hydroxide and 12-Hydroxystearic acid (12HSA) and their precursors, will need to be registered. The timeframe at which they have to register will again be determined by their volume level. The manufacturers of these chemicals will also need to support their use in manufacture of a soap thickener.

FIG. 3 SOAP THICKENER – INFORMATION FLOW



The Lithium soap is normally manufactured in-situ by the grease formulator. This makes the grease formulator the manufacturer of this chemical and responsible for REACH and any registration actions. As this level is likely to exceed 10 tonnes p.a., then all downstream uses of the soap will need to be assessed using exposure scenarios, the risk determined and risk management advice communicated to all users. The import of the same soap or a formulation containing the soap, from outside of the EU will trigger registration obligations on the importer for each substance in the formulation if they exceed the minimum threshold for registration.

BASEFLUID

In order to manufacture an ester basefluid the individual chemicals (acids, alcohols, process chemicals) used in manufacturing would have to

load carrying capacity of a properly formulated grease can be achieved by the lubricant film itself. Extreme pressure additives should therefore only be expected to function in acute situations and to provide additional security. Under such circumstances, the lubricant film thins out and metal to metal contact can occur; this usually happens at elevated temperatures, at reduced operating speeds or during extreme high loading. The distribution of lubricating grease becomes uneven in the contact zone and metal asperities come together causing even more heat and dramatically increasing friction.

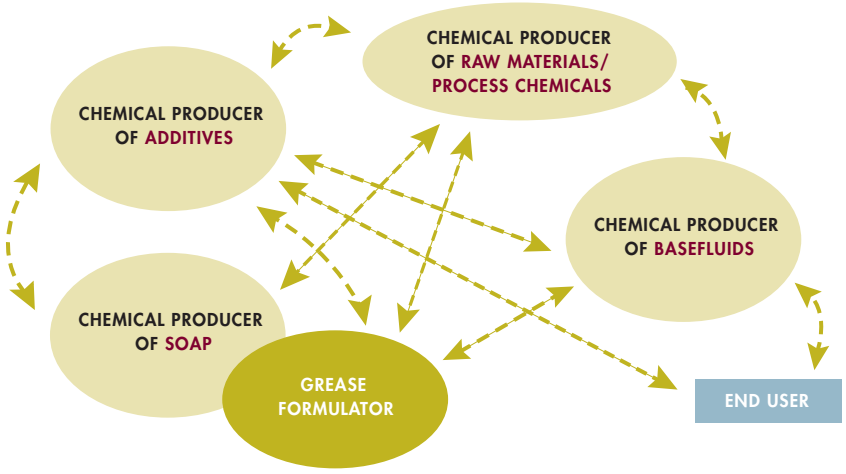
All extreme pressure additives need therefore to be highly reactive at the metal surface. When the local temperature rises above a certain critical level, they react and change the chemistry of the metal surface. With most conventional extreme pressure additives, the high spot becomes brittle and simply breaks off. Other additives change the hardness of the metal creating smoother surfaces. These micro-mechanisms stop the surfaces from welding together.

More traditional additives, based on lead, have already been replaced by compounds of sulphur and phosphorus, and these are, in turn, being replaced by more environmentally acceptable products.

ANTI-WEAR ADDITIVES

Although they are similar in function to their extreme pressure counterparts, anti-wear additives operate at

FIG. 4
FORMULATED PRODUCT-INFORMATION FLOW



go through the REACH process. In addition the ester manufacturer or importer will have to register this ester under REACH and to ensure all known uses of the ester are identified and supported in the chemical safety assessment – assuming the manufacture or import is greater than 10 tonnes p.a.

ADDITIVES

In order for a grease to perform in-service we also need to include some performance additives. These are necessary additives rather than optional and perform a key role in grease performance and longevity. Each of the chemicals used as an additive or in a formulated additive package will have to be registered in REACH unless again the quantity manufactured or imported by each supplier is less than 1 tonne p.a. (except the viscosity improver or antifoam which, normally as a polymer will initially be outside of scope of REACH).

CONCLUSION

Figure 4 shows how the information flow required for a complete end formulation.

The likely consequences of REACH on grease formulation are significant. They may include increased costs of raw materials as the financial impact passes down supply chains; the potential loss of raw materials and the effect not only on future formulation but on existing ones – this will require a re-direction of R&D resources to future proofing formulations; the potential loss of supplier choice and inevitable consequences on availability and cost; and although this has not been covered in detail – the impact of the extended controls on

lower temperatures and under less stressful conditions. These materials normally work by forming some kind of protective mono-molecular film on the metal surface often by physical adsorption. Thickeners based on metal soaps can actually provide a certain degree of anti-wear protection and, like soaps, many anti-wear additives are actually based on long chain, fatty molecules. Such types of additives can also be used as friction modifiers to optimise performance under less critical conditions.

TACKIFIERS

In order to increase adhesion towards metal surfaces, tackiness additives are often incorporated into grease formulations. These are mostly different types of synthetic polymers but other materials such as rubbers and natural latex are also commonly used. A more recent development is the incorporation of so-called functional polymers into the thickener structure thus improving the adhesion of the soap itself. This is especially effective in wet applications. One common mistake is to use additives which increase the cohesive instead of adhesive properties of the finished product but this only serves to make the grease like chewing-gum, increasing internal friction and impeding lubricity.

SOLID LUBRICANTS AND ANTI-SEIZE COMPOUNDS

A comprehensive range of different materials are used for these purposes, but the following are typical in many applications: graphite, molybdenum disulphide,

substances of high concern and the authorisation obligation to permit continued use.

The potential implications of REACH on all parts of the supply and use chain, even those well down the supply chain are beginning to be realised especially by the automotive industry. A number of the issues emerging are associated with loss of raw materials and more specifically, the potential loss of raw materials in Europe and what impact this will have on global formulation trends.

The question of confidentiality and loss of confidential business information remains a key concern to the formulation industry. The obligation to disclose and communicate on composition during the registration process and down through supply chains have been identified as risks to formulation identity and composition leading to the increased likelihood of reverse engineering and loss of proprietary information.

The ultimate scope and form of REACH may change, however it is inevitable that such a reforming legal measure will result in significant changes in the chemical industry, to downstream users of these chemicals and then further down the supply chain.

In order to prepare for REACH companies should compile an inventory of individual chemical substances and preparations (with suppliers listed) and establish whether these are manufactured by your company within the EU, imported by your company into the EU or purchased by your company from a supplier established within the EU. The information available (in-house or public domain) for these substances should be reviewed especially for the substances requiering registration by your company rather than by the supplier.

All the readily available information on uses and conditions of uses for the substance or preparation should be compiled. This information should include broad use categories as industrial use, professional use or consumer use.

References

1. COM (2001) 88. White Paper – Strategy for a future Chemicals Policy.

2. COM (2003) 644. Proposal for a Regulation of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (Reach), establishing a European Chemicals Agency and amending Directive 1999/45/EC and Regulation (EC)

3. Reach Implementation Project 1 (RIP 1). June 2004. REACH Process Description: Development of a detailed description of the REACH processes.

4. The Sport Report (Strategic Partnership on REACH testing) July 2005 – Making REACH work in practice.

5. For more information http://europa.eu.int/comm/enterprise/reach/index.htm

calcium carbonate, zinc oxide, borax, various metal salts, ceramics, clays, PTFE and other plastic polymers, copper powder and zinc powder.

Many solid lubricants and anti seize compounds can be used at very high temperatures indeed, in continuous operation well above 200°C, where normal grease systems fail due to oxidation and evaporation. In some cases, the solid lubricants are delivered to the machinery surfaces by some type of gelled system, and the "grease" itself is simply a carrier. For extremely high temperatures, this can be, for instance, a polyglycol which evaporates completely, leaving behind the solid material on its own to ensure sufficient surface separation.

Some of these additives are also used when the grease is required to display special degrees of electrical conductivity or heat transfer properties.

The most important use of the more conventional types of solid lubricants such as graphite and molybdenum disulphide is in applications where equipment design does not allow the formation of a hydrodynamic lubricating film. The solid lubricant is then expected to act as a simple mechanical barrier between the operating surfaces. This type of lubrication is required for heavy shock loading and under oscillating conditions mainly found in construction equipment and very heavy industry.

In the next issue of the White Papers we will address the challenges and opportunities for the new generation of environmentally friendly greases.

As usual we encourage our readers to give us feed-back and requests for grease technology topics they want us to cover in future Lubrisense White Papers.

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