RECO-COOL

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Glycol's Toxicological and Environmental Considerations

BACKGROUND

There has been considerable discussion in the marketplace about the use of Propylene Glycol (PG) based coolants versus (Mono-)Ethylene Glycol (MEG) based coolants. This bulletin discusses the merits of both fluids in the formulation of antifreeze/coolant products, with particular emphasis on the environmental and toxicological differences between the two.

MEG based coolants have dominated the antifreeze/coolant market since their first inception midway through the 20th Century. The performance of MEG as a formulary base fluid in coolants is well known. It has a favourable effect on the reduction of Freezing Point (therefore the first choice ingredient in cold climates), and also has a beneficial (less marked) effect in raising Boiling Point. MEG is relatively easily available, has excellent heat transfer properties and, whilst more expensive than water, is a relatively cost effective means in enhancement of fluid characteristics of coolants. MEG is also highly biodegradable, and standard performance production specifications easily accomplish the technical requirements for coolants.

PG in contrast is only relatively newly introduced in the market as a formulary base fluid for coolants, although its performance as such has been well studied for many years. Essentially (because of the similarity of the molecules) the performance of PG in typical performance characteristics is very similar to MEG, albeit slightly poorer performance in a number of metrics. PG, too, has a favourable effect on the reduction of Freezing Point (albeit lesser than MEG), and a beneficial effect in raising Boiling Point (again, lesser than MEG). It is also highly biodegradable (again, less so than MEG), and has excellent heat transfer properties (once again, less so compared to MEG). In each of these parameters, PG offers good performance but not as good as MEG. In contrast

to MEG, PG is a specialised fluid with a unique market and is consequently significantly more expensive. Its use in antifreeze/coolant preparations and formulations will inevitably lead to an increase in cost.

Perhaps the most striking difference in the two fluids, PG vs MEG, is the relative toxicology. Where MEG is generally regarded as toxic, PG is in effect non-toxic and is frequently used in applications requiring a “food grade” coolant (such as refrigerants) where incidental food contact is possible.

This bulletin explores these toxicological differences fully. Further discussion on the environmental differences is also included.

In addition to evaluating MEG and PG, we also include a number of derivative glycols in this discussion as well, although these fluids are almost unheard of in use in automotive coolant formulations.

TOXICOLOGICAL CONSIDERATIONS

ACUTE ORAL TOXICITY

All of the glycols considered in this booklet display a low acute oral toxicity in laboratory rats. The accompanying table lists the LD^{50} * values obtained when the various glycols are fed in single oral doses to rats.

LD^{50} Values for Various Glycols Single Doses to Rats

Glycol	LD^{50} gm/kg
Ethylene (MEG)	6.1
Diethylene	16.6
Triethylene	22.0
Tetraethylene	32.8
Propylene (PG)	33.7
Dipropylene	14.8
Tripropylene	3.0**

** The LD^{50} (Lethal Dose, 50%) is the smallest dose of sample that will cause death in 50% of a sample of rats. The lower the number, the more toxic the fluid sample*
*** Largest dose survived by all rats tested: I 0.0 gm/kg resulted in the death of all the rats tested*

Human experience indicates that man seems to be more susceptible to injury caused by glycols than laboratory animals. For example, the lethal dose for humans for MEG appears to be about 1.56 gm/kg (1.4 ml/kg), about a quarter of that for rats.

CHRONIC ORAL TOXICITY

Different glycols vary considerably in chronic oral toxicity. PG is especially low in this respect; studies in which rats were fed drinking water containing as much as 10% PG over a period of 140 days showed no apparent ill effects, while other investigations have revealed that rats can tolerate up to 4.9% PG in the diet for 24 month periods without significant effect on growth rate. However, minor liver damage was observed. Because of its low chronic oral toxicity, PG is considered safe for use in foods and pharmaceuticals. Since 1942, it has been included in New and Non-Official Remedies as a proper ingredient for pharmaceutical products and is listed in the United States Pharmacopoeia. It is widely used and accepted as an ingredient of dental preparations and is considered generally recognized as safe for use in foods if used in accordance with good manufacturing practices.

In contrast, MEG is regarded as too toxic for applications where there is a possibility of ingestion. Feeding rats for two years on diets containing 0.5 and 1.0 gm/kg of ethylene glycol caused a toxic action centred chiefly in the kidneys. MEG ingestion shortened the life span of the rats, produced calcium oxalate bladder stones, severe renal tubular atrophy, and fatty degeneration in the liver.

USE OF BITTERANTS IN ANTIFREEZE/COOLANT FORMULATIONS

In order to minimise the risk of deliberate or accidental ingestion of antifreeze/coolant products, many countries have stipulated the mandatory inclusion in the formulation preparation of DENATONIUM BENZOATE which is a pungent and bitter additive causing pharyngeal spasm (ie gag-reflex) in humans. If coolant containing such additive is ingested (by humans or most animals) then further ingestion and digestion will be prevented.

Formulations containing this additive manage the high Oral Toxicity of MEG through subsequent formulation management. This is generally considered a

lower cost option, and preferred performance option, than replacing the MEG with PG for these types of products and applications.

Most 1st world governments have introduced mandatory minimum concentration levels of DENATONIUM BENZOATE in automotive coolants for this reason. Concentrations of DENATONIUM BENZOATE required are typically <40ppm.

EYE AND SKIN CONTACT

All of the glycols, including those high in Oral Toxicity (such as MEG), produce a negligible degree of irritation upon eye or skin contact. A slight macerating action comparable to that caused by glycerine may result from very severe prolonged exposures. There is no evidence to indicate that they are absorbed through the skin in quantities sufficient to produce systemic injury in normal industrial handling. If severe exposure to ethylene glycol or diethylene glycol occurs, it is possible that enough of the material might be absorbed to cause systemic injury. Because of these considerations, the use of ethylene or diethylene glycol in preparations intended to be applied over extensive areas of the body is not recommended.

VAPOUR INHALATION

Inhalation of the vapours of the glycols appears to present no significant hazard in ordinary applications. Human experience and animal data have provided sufficient basis for setting a threshold limit value of 50ppm ceiling for the vapours of MEG and a value of 10 milligrams of MEG as particulate matter such as mist in one cubic meter of air (10 mg/cu.m). Mist and aerosols, or high concentrations of vapours at elevated temperatures, of MEG may pose a hazard to humans. Having said this, automotive antifreeze/cooling systems are fully enclosed (or should be) and normal maintenance practices stipulate that fluids should only be changed when the system is cooled. This suggests that the risk of vapour inhalation of MEG is very low, and the risk of long term exposure is negligible.

Adequate ventilation should always be provided to control the mists or vapours of MEG to the threshold limit values set when handling the fluid at elevated temperatures is unavoidable.

ENVIRONMENTAL CONSIDERATIONS

BIODEGRADATION

The primary glycols, MEG and PG, are expected to be readily biodegradable and thus will not remain in the environment. The data in the chart below and numerous scientific studies indicate that except for tripropylene glycol, biodegradation is expected to be moderate to high under both aerobic and anaerobic conditions for all the glycols. There is substantial information in the literature concerning the biodegradability of glycol compounds.

Biodegradation		
Glycol	ThOD	BOD-20 Day
Ethylene	1.29p/p	1.15p/p
Diethylene	1.51	0.88
Triethylene	1.60	0.27
Tetraethylene	1.65	0.71
Propylene	1.68	1.45
Dipropylene	1.91	0.71
Tripropylene Glycol	1.38	-

AQUATIC TOXICITY

MEG and PG are both considered to be practically non-toxic to fish on an acute basis (LC^{50}*> 100mg/L) and practically nontoxic to aquatic invertebrates on an acute basis (LC^{50}> 100 mg/L).

**The LC^{50} (Lethal Concentration, 50%) is the smallest concentration of sample in an aquatic system that will cause death in 50% of a sample of fish. The lower the number, the more toxic the fluid sample.*

GENERAL CONCLUSION

The toxicology of a number of different Glycols has been discussed in this Bulletin. Under appropriate handling, all Glycols should present no serious hazard insofar as their normal industrial handling and use are concerned.

MEG has high acute and chronic oral toxicity. This is considered low risk in automotive antifreeze/coolant preparations, and most 1st world governments have introduced mandatory use of DENATIONIUM BENZOATE to minimise the risk of ingestion.

The alternative of replacement of the MEG with PG is possible, albeit a higher cost alternative. The resultant PG-based automotive fluid has poorer Freezing Point, Boiling Point, Heat transfer and biodegradability compared to the same fluid with equivalent concentration of MEG.

DISCLOSURE

Recochem has published LD^{50} and LC^{50} test results in this bulletin which have been sourced from a number of reference sources on the internet (available upon request). Recochem does not advocate nor has ever conducted live animal testing of our products.