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**ANALYSIS OF THE POSSIBILITY OF USED COOLANT
REGENERATION****Key words**

Coolant, regeneration, glycol, water, membrane techniques.

Abstract

The paper presents the problem of the regeneration of coolants used in industrial cooling systems by investigating physic-chemical properties of used coolants and solid particle content. It was found that the used coolant is contaminated with solid particles, products of condensation, chemical products of the fluid's aging process, products of corrosion, and elements of the cooling system. This contamination of fluids prevents its regeneration by relatively simple methods that can be implemented by a user. It is possible to recover glycol and optionally water from the used coolants. Currently, the most suitable methods for regeneration are hybrid membrane techniques.

Introduction

EU observes regulatory procedures for environmental protection. They concern the pollution emission from manufacturing processes. As a result, the EU attaches great importance to the development and application of environmental technologies. It is compatible with the idea propagated in “worldwide cleaner production.” Its essence is to reduce energy consumption

and the closing of the primary and secondary circuits of the materials used in production processes [1]. This idea involves all working fluids.

A common feature of working fluids is that their value is relatively small compared to other manufacturing costs. In operating conditions, the fluids undergo deterioration, an increase the concentration of undesirable products of aging, and the fluids stop fulfilling its operational function. The used working fluids should be regenerated or replaced by new [2]. Replacement costs for coolants is less than the cost of their regeneration. Users are not encouraged to close the circuit of coolants and to manage them rationally. In these circumstances, an effective way of getting users to the rationalization of operating coolants may be a legislative action. The need to meet regulatory requirements may cause an increase in the overall cost of production and a decline in price competition of EU products on the global market.

Solving technological problems associated with closing circuits of coolant use are not conducive to fluid manufacturers who are interested in the highest possible sales. Environmental problems are exposed in their marketing strategies, but the real action in this area are often branded. Therefore, the key research centres in the country and abroad are currently trying to develop a low-cost and efficient recycling and recovery technology of various raw materials used in the industry, including working fluids. Developing fluid technologies should be advanced enough to be able to implement them directly in a potential application [2].

Some of the commonly used working fluids whose consumption is steadily growing are coolants. They are heating (or cooling agents) in all kinds of devices needing heat abstraction or supply during operation.

The main consumer of coolants is in the automotive industry. Depending on the size and power of the engine, a cooling system contains up to dozens of litres of such coolants. The production of such coolants using a relatively low-cost raw materials, such as water and ethylene glycol, or less toxic, but more expensive, propylene glycol, are predominant [2, 3]. A mixture thereof, usually in a ratio close to 1:1, is enriched with small amounts of anti-corrosion, passivation, bacteriostatic and foam inhibitors, and colorants (for marketing). During operation, additives wear out and the fluid is contaminated, so it is replaced in accordance with the criteria established by the engine manufacturer. The service personnel deal with the collection of waste automotive working fluids. Glycol or coolant manufactures deal with their recycling [3, 4].

Coolants are a heat-transfer medium and are becoming more widely used in heat pumps and solar systems. There is an annual increase in the number of these installations in Poland [5]. As in the case of vehicles, users of such facilities are also dispersed. Any uncontrolled emission of fluids in the environment can cause devastating ecological consequences. To reduce such

risks in these systems, fluids based on less toxic propylene glycol [2, 3] are used.

Large amounts of coolants are used in central heating systems (especially in large office buildings, technical or manufacturing plants), and cooling systems in industrial objects and air-conditioning units. They have been in widespread use in the food industry, where production facilities are often air-conditioned, and where there are large refrigerated warehouses [5]. Because of the potential danger of contact of the fluids with food, propylene glycol containing fluids are almost used exclusively in the food industry systems [2]. This is due to the legal acts adopted in the EU related to food production and to technology and refrigeration and air conditioning security. These regulations include the following:

- Regulation (EC) No 178/2002 of the European Parliament and of the Council of 28 January 2002 laying down the general principles and requirements of food law, establishing the European Food Safety Authority and laying down procedures in matters of food safety (OJ. Communities L 31 of 01.02.2002, page 1; Gazette. Polish special edition, ch. 15, vol 6, p 463).
- Regulation (EC) No 852/2004 of the European Parliament and of the Council of 29 April 2004 on the hygiene of foodstuffs (OJ. L 139, 30/04/2004 p 0001-0054), which sanctioned the so-called. HACCP (Hazard Analysis and called Critical Control Point System). HACCP is a system of which conduct is aimed at identifying and estimating food safety hazards, from the point of view of the quality of care and the risk of these hazards at all stages of production and distribution. It is also a system designed to identify methods of reducing these risks.
- ISO 22000:2005 – Food Safety Management System for organizations in the food chain. This standard combines the HACCP system and a system of good practice and is addressed to all organizations which, through there are activities engaged in the production, processing, storage, transporting and marketing of food.
- Regulation (EC) No 853/2004 of the European Parliament and of the Council of 29 April 2004 laying down specific hygiene rules for food of animal origin (OJ. EC, L 139/55, 2004).
- Opinion of the European Economic and Social Committee on The Principles of hygiene and processing craft (2006 / C 65/25).

While working in cooling and air conditioning systems, coolants undergo deterioration, leading ultimately to the generation of hazardous waste [5]. However, there are no assessment standards for using coolants. There are only standards of fluid qualifications for automotive vehicles, e.g. Polish Standard PN-C-40007:2000 “Coolants for cooling systems of engines, Requirements, and testing methods” used in assessing the quality of fresh automotive coolants [6].

However, taking into consideration the similar composition and functions of automotive coolants and fluids for cooling and air conditioning systems, the latter can be effectively tested in accordance with the methods described in the PN-C-40007: 2000. Nevertheless, assessing the condition of the coolants during operation phase remains an unsolved problem.

In the absence of a system to assess the current operational state of the coolants, it becomes understandable that there is no system of regeneration. This problem needs an effective solution. During operation, coolants may significant changes in their chemical composition and physical properties [5, 6]. From analytical data, the following components have been identified in used coolants: benzoates, oils, nitrites, amines (nitrosoamines), borates, silicates, heavy metals (Pb, Fe, Cr, Zn, Sn, Cu), and others, such as different aromatic compounds [6]. For these reasons, the used coolants were incinerated; however, due to the high water content, the process is uneconomical. Therefore, recovery of glycol from the used coolants is preferred [5]. Due to the complex composition of the waste and problems with traditional recycling, hybrid membrane technologies are used for the separation of glycol from the used coolants are undertaken [7, 8, 9,10].

The aim of this study is to evaluate the possibility of the regeneration of used coolants operating in cooling and air conditional systems in the food industry using membrane techniques.

Experimental

Objective of the investigation was a coolant used in a cooling system for the food industry. It was used in meat processing plants for about a year (between periodic inspections of the installation). The fluid contained water (45%v/v), propylene glycol, and some additives (corrosion inhibitor, pH control agents, and alkali reserve materials).

The prepared samples were new and used coolants as well as a solution (10% v/v) of the used coolant in isopropyl alcohol. The used fluid was diluted in the isopropyl alcohol with the aim of dissolving oligoglycols and eliminating the influence of substances on the mass of solid impurities. During the calculation of the content of the impurities in samples, it was taken into consideration that the used fluid was diluted.

The following properties of the prepared samples were investigated: density, index of refraction, solid particle content, pH, alkali reserve, colour, corrosive effect on ferrous metals, and microbiological contamination.

1. Investigation procedures

Density was determined at 20°C, according to Standard PN-EN ISO 12185:2002, by automatic density meter *DMA 4500M* from *Anton Paar*. The measurement was based on the oscillating U-tube principle ensuring highly accurate density values ($\pm 0.00005 \text{ g/cm}^3$).

Index of refraction was determined at 20°C according to Polish Standard PN-C-04952:1981, by Abbe refractometer *Abbemat 350* from *Anton Paar*.

Solid particle content by mass concentration was determined according to PN-ISO 4405:1994P intended for the hydraulic fluids. Application of the test method is proper in the absence of the method intended for coolants and physical properties of both types of fluids are similar. Moreover, air conditioning and refrigeration systems are similarly sensitive to the effect of solid particles. The PN-ISO test method was insignificantly modified. In order to determine the total content of solid impurities and mass fraction of particles, the sample used for analysis (500 cm³) was filtered through three different filters (pore sizes were 5; 1.6 and 0.8 μm respectively).

pH was measured by direct potentiometry according to PN-C-40008-04:1992P. The measurements were performed by means of digital pH-meter (*Crison Instruments*, model *MM 41*) equipped with a combination electrode with built-in automatic temperature compensation.

Determination of *alkali reserve* according to PN-C-40008-05:1993P was done with the use of automatic titrator *Crison TitroMatic*. We performed potentiometric titration of 20 cm³ of the sample with a 0.1 n hydrochloric acid solution to reach pH = 5.5. Then we determined the volume of the solution required to titrate the sample. A pH value of about 5.5 corresponds to the equivalence point of a borate buffer (borate buffers are commonly used to blend traditional coolants). However, it does not agree with the equivalence point of the buffer based on organic acids. (Such buffers are used to produce a new generation of coolants. Depending on the type of organic acids, pH can even reach values of 3). Therefore, the determination of the alkali reserve for pH = 5.5 is a rough estimate. In the absence of a buffering method for the investigated coolant, the alkali reserve was determined in the same way as borate buffer.

Colour of the samples was determined according to PN-C-04037:1975 by means of *Hach DR/4000* UV-VIS Spectrophotometer. Absorption of radiation was measured at 530±2 nm (in relation to absorbance measurement for distilled water).

The corrosive effect on ferrous metals was examined as described in PN-M-55789:1992P (Herbert test method). Cast-iron plates and steel chips have been immersed in the sample of coolant and kept at 23±5°C for 24 hours. The corroded surface of the plate was calculated as a percentage of total surface area.

To determine *microbiological contamination*, a dip slide test was conducted. Dip slides were incubated at 30°C for 48 hours after being dipped into the sample. Bacteria (agar base) as well as yeasts and fungi (glucose base) present in the sample were growing and forming colonies. Then the number of bacteria, yeasts, and fungi in the sample was determined.

All measurements were repeated three or more times. Potential outliers were removed using Dixon's Q-test (at 0.90 confidence level). The result was calculated, after the rejection of outliers, as the arithmetic mean of three significant values.

2. Results and discussion

Table 1 presents the basic physic-chemical properties of new and used coolant as well as a solution (10% v/v) of the used coolant in isopropyl alcohol. As seen in Table 1, during operation, there was a slight change in the index of refraction values of the coolants indicating that the ratio of water to operated glycol fluid did not change significantly. The liquid can be further exploited with this degree of corrosion and microbiological contamination. However, the lesser colour change, and the reduction in the acidity of alkaline reserve indicate that a part of liquid components had worn out and the products of chemical glycol transformations had appeared. Therefore, continued operation of the liquid without adjustment of its properties can be risky [3, 5]. Alkaline reserve and pH of the used liquid can be easily improved by introducing the respective amounts of such additives that are used in the preparation of new liquid. However, in order not to cause precipitation of some of the liquid ingredients, the same additives were used in its preparation. Procedures that are more complicated are required to correct the colour of the liquid in service, but this can be achieved by absorbing impurities at an appropriate adsorbent. However, this will trigger the absorption of other components, and it will deepen the liquid chemical changes and the formation of waste (spent adsorbent), making it difficult to treat.

Table 1. Physic-chemical properties of new and used coolants

Parameter	Fresh coolant	Used coolant	Solution of the used fluid in isopropyl alcohol
Index of refraction	1.3755	1.3790	1.3775
colour, B ₅₃₀	2.34	5.18	4.23
Density at 20°C [g/cm ³]	1.054	1.062	0.832
pH	8.85	7.75	7.67
Degree of corrosion [%]	0	0	0
Alkali reserve [cm ³ 0.1 n HCl]	9.4	7.0	6.25
Microbiological contamination	not indicate	not indicate	not indicate

An important parameter indicating the status of used coolant is the degree of the contamination of solids particles. At the same time, the size of these

particles is important. Therefore, in addition to the total content of impurities (cut-off limit of 0.8 μm), the content of impurities larger than 5.0 μm and in the range of 1.6 to 5.0 μm s and 0.8 to 1.6 μm was also examined. Whether some of these contaminants (resulting from aging of a liquid) can be soluble in isopropyl alcohol was also examined. The degree of contamination of new and used coolants can be assessed based on the data presented in Table 2.

As is clear from the data presented in Table 2, even unexploited coolants is not free from impurities solids. However, during the exploitation, their content significantly increases and solid particles sizes larger than 5 μm appear in used fluid. Among the particles of this size, only a small number of them represent the portion soluble in oligomers of isopropyl alcohol. The proportion of organic particles with a size of 0.8–5.0 μm is greater than of particles > 5.0 microns. It can be suppose that the organic components were mounted on mineral particles; therefore, after digestion in isopropyl alcohol, the total amount of pollutants and impurities in different size groups in the test liquid decreased. Most installations are harmful to a particle size > 5.0 μm . Hard mineral particles of this size will accelerate wearing of the heat-exchange system components. The same size polymer particles may even protect the system against wearing out.

Table 2. Solid particle content in samples of the coolant

Filter pore size [μm]	Solid particle content in the samples [g/dm^3]		
	fresh coolant	used coolant	solution of the used fluid in isopropyl alcohol
5	0.000	0.584	0.500
1.6	0.032	0.446	0.336
0.8	0.196	0.492	0.345
Σ	0.228	1.542	1.181

Particulates contaminating coolants during operation can be formed in the heat-exchange system or penetrate into it from the outside. The penetration of impurities from the outside can usually be substantially reduced or eliminated. Impurities generated in the heat transfer system may be the result of the consumption of the installation itself, as well as the aging of coolants. Removing impurities from the liquid on a daily basis involves costs and the loss of energy. In addition, the presence of the soft particles in the liquid oligomeric partition hinders the use of filters, since they are subject to rapid blockage.

Determination of the physic-chemical properties of the coolants and analysis of the literature data made it possible to determine the nature of the aging changes of the liquids and propose how to proceed with it. Because of the aging chemical contaminants, e.g. carboxylic acids [11], which are capable of condensation and lead to the formation of oligomers or polymers, may be formed alternately. In addition to changes resulting from the contamination of

the liquid components, there are unwanted materials created by the wear and probably corrosion of system components. Although there were no microorganisms in the test samples, their development cannot be excluded during the long service life of the liquid in the cooling system, especially in areas of slow fluid flow.

Taking into account the results of the research and published data [9, 12], it can be concluded that the possibility of regeneration of the coolants using glycol is virtually nil. This is because there are significant chemical changes to the liquid itself that are impossible to reverse in a simple technological process. The only and sure way to re-use exploited liquid is to recycle its basic components [4]. The most valuable of these is the glycol. In practice, there are several ways to recycle glycol from coolants [8].

The standard technical scale process for glycol recovery from coolants is a multi-stage distillation performed at atmospheric or reduced pressure [8]. In the first stage, the water content of 60–80% is reduced, followed by a thin film evaporator separating the glycol as the overhead product from the waste concentrate, which contains a low vapour-pressure species, such as heavy metals, oil, corrosion protection agents, and decomposition products. These residues have to be sent for final hazardous waste treatment, such as waste disposal or incineration.

Effective separation of glycol can be done by hybrid membrane techniques, in particular pervaporation and reverse osmosis [8]. The proceedings in this case can be divided into several stages as follows:

- Pre-treatment consisting of the separation of solids and large particles in the microfiltration and ultrafiltration techniques cross-flow.
- Glycol dehydration by evaporation to a level of about 30%, comprising a water – the process temperature can be kept far below the typical temperature of the engine cooling system, avoiding the formation of nitrosoamines.
- Pervaporation, nanofiltration, and reverse osmosis is in conjunction with evaporation for further concentration. The product of pervaporation is retentate, which is a highly concentrated glycol liquid (> 95%), but it still contains the additives of the coolant liquid and their decomposition products. Further purification of glycol is carried out in a multistage process of nanofiltration and reverse osmosis, which allows it to reach a concentration of about 99.5%. Reverse osmosis (RO) is used for the final treatment of the water fractions. The permeate (< 0.05% glycol) is ready for direct discharge into the sewage system. The retentate (> 5% glycol) is transferred back into the EV for further concentration.

Membrane processes implemented in such a sequence enable energy efficiency while recovering glycol from coolants.

At the present state of development, the membrane hybrid process [8, 10] already offers economic recovery of ethylene glycol from used coolants.

Conclusions

Based on the literature review and knowledge of physic-chemical properties of the glycol-based coolant, it has been shown that regeneration of this type of fluids by relatively simple methods is practically impossible. Even the simplest barrier filtration could become useless in view of the presence of condensation products in the used fluid (the products block barrier filters). The effective solutions to the problem are hybrid membrane techniques, including cross-flow microfiltration, nanofiltration, and reverse osmosis realized under suitable hydraulic conditions. When selecting a type of membrane, it is necessary to take into consideration the properties of the used fluid, the purpose of the process, and its expected performance.

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Analiza możliwości regeneracji zużytych cieczy niskokrzepnących

Słowa kluczowe

Ciecz niskokrzepnąca, regeneracja, glikol, woda, techniki membranowe.

Streszczenie

W artykule przedstawiono problematykę regeneracji przepracowanych cieczy niskokrzepnących z układów chłodniczych instalacji przemysłowych. Dokonano oceny właściwości fizykochemicznych eksploatowanej cieczy niskokrzepnących oraz zbadano zawartość w niej zanieczyszczeń stałych. Stwierdzono, że eksploatowana ciecz jest zanieczyszczona cząstkami ciał stałych, produktami kondensacji, chemicznymi produktami starzenia jej składników oraz produktami korozji elementów instalacji chłodniczej. Tak różnorodne zanieczyszczenie cieczy uniemożliwia jej pielęgnację względnie prostymi metodami, możliwymi do realizacji u użytkownika. Ze zużytej cieczy niskokrzepnącej możliwy jest jedynie odzysk glikolu i, ewentualnie, wody. Obecnie najbardziej odpowiednie do tego celu są hybrydowe techniki membranowe.