
Project C

Survey of Environmental Restrictions to the Use of Additives in District Heating and Cooling Systems

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CONSULTING ENGINEERS,
ECONOMISTS AND PLANNERS



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Contents

1. Introduction	1
1.1 Background	1
2. The survey	3
2.1 Basis	3
2.2 Relevant additives	3
2.3 Transport, storage and handling of the additives	4
2.4 Authorities.....	4
2.4.1 Rules reported.....	4
2.4.2 Level of authorities	5
2.4.3 Criteria.....	5
2.4.4 Demands still to be fulfilled	6
2.4.5 Status of permission	6
2.5 Conclusion	6
3. Appendix	7
3.1 Questionnaire.....	7
3.2 EC safety data sheet for Dobon-G.....	10

1. Introduction

The purpose of this project was to provide a survey of restrictions and approval procedures for the use of additives such as friction reducing agents and phase-change materials in district heating and cooling systems in various countries.

The survey was based on a questionnaire distributed to the members of the IEA Advanced Fluids Expert Group at the beginning of 1995.

The target group for the survey is:

- The potential users of advanced fluids, i.e. district heating and cooling utilities,
- The manufacturers of additives,
- National, regional and local authorities involved in the approval of the use of the additives,
- The expert group.

1.1 Background

For more than 10 years an extensive research and test programme concerning the use of additives for district heating and cooling systems has been carried out in various countries.

As an example technical subjects related to the use of friction reducing agents Habon-G and Dobon-G have been examined in laboratory and field tests as well as theoretical studies with the conclusion that there are no serious technical problems in relation to the use of these additives in district heating systems.

One main issue, however, remains to be clarified before a full-scale application and commercial availability can be foreseen, namely the environmental restrictions related to the use of these additives. The reason for this is that the additives are slightly toxic although not more harmful than many surfactants used in industry and households.

The greatest concern to the use of additives is attached to the possible leakage to the surroundings (drinking water resources) and the risk of contaminating consumers' hot sanitary water. These subjects therefore are some of the main obstacles for the use of additives in district heating and cooling systems.

Already at an early stage it was therefore recognized by the expert group that the use of friction reducing agents in district heating systems should be limited to primary heat transmission systems, which are hydraulically isolated from distribution networks, only.

It was therefore considered important to examine the attitude of the authorities toward this subject in various countries in order to evaluate the future possibilities for using this type of additives at a large scale.

On this background Bruun & Sørensen Group AS presented a proposal to the expert group on the execution of this survey and was appointed to carry out this task. The report was written by Mr. Flemming Hammer.

2. The survey

A questionnaire was distributed to all members of the expert group, and replies have been received from the following countries: Canada, Finland, Denmark, Germany, Korea, The Netherlands, Sweden and the USA. A copy of the questionnaire with the answers given by B&S for Denmark is in the appendix.

2.1 Basis

The first questions relate to the basis on which the replies are given.

Most of the information is based on general knowledge or informal contacts between individual members of the group and representatives from local, regional or national authorities.

In Germany and Denmark where concrete full-scale tests have been conducted in a total of six cases, which demanded approval from authorities, concrete experience has been gained, and is reflected in the answers.

Each country indicated the following basis of their answers:

General knowledge - no contact with authorities	Korea, USA
Some informal exchange of information	Canada, Finland, The Netherlands, Sweden
Application under preparation	Sweden
Application delivered	-
Permission with restrictions obtained	Denmark, Germany
Permission obtained without restrictions	-

2.2 Relevant additives

A number of substances have been used for small-scale testing in Canada, Germany, The Netherlands, Sweden and the USA. Large-scale field test were only made with the additives from Hoechst AG; Frankfurt, Germany (Habon), Habon-G and Dobon-G, the latter in conjunction with sodium salicylate. These additives are for district heating.

Habon-G (n-alkyldimethylpolyoxethylammonium, n=16) fits to the temperature conditions used in Herning, Denmark (40-100°C). The concentration used in order to obtain the maximum effect has been 150-250 ppm.

Dobon-G mixed with sodium salicylate n-alkyldimethylpolyoxethylammonium-3-hydroxy-2-naphthoate, n=20-22) was used in Völklingen, Germany, where the temperature level is 40-130°C. Concentration of Dobon-G 1500 ppm + sodium salicylate 700 ppm.

These additives are registered chemical substances in the EU-countries.

The following additives for district cooling have been submitted for approval to be imported or manufactured in Canada. They are active in the temperature range of approx. 0-30°C:

- Octadecyltrimethylammonium chloride**,
- Cetyltrimethylammonium bromide (hexadecyltrimethylammonium bromide)*,
- Dodecyltrimethylammonium bromide (or chloride)*,
- Octadecyl-bis-(2-hydroxyethyl)-methylammonium chloride**,
- 9-octadecen-bis-(2-hydroxyethyl)-methylammonium chloride**,
- Myristiltrimethylammonium bromide (or chloride)**.

The following additives, to be used as counter ions at a concentration of some 400 ppm have temporary approval for import/manufacture but will have to go through a more detailed review in the next year before being finally approved:

- 2,6-dihydroxybenzoic acid (α -resorcylic acid)*,
- 3-methylsalicylic acid (2-hydroxy-3-methyl-benzoic acid or cresotic acid)*.

* Available from Aldrich Chemical Co., Milwaukee, Wisconsin, USA

** Available from Akzo Chemicals Ltd., Toronto, Ontario, Canada

2.3 Transport, storage and handling of the additives

Hoechst AG has submitted EC safety data sheets complying with 91/155/EEC for Habon-G (Hoe 4089) and Dobon-G (Hoe 3987) (Appendix).

2.4 Authorities

These questions refer to the formalities which have been met by the contacts to the relevant authorities.

2.4.1 Rules reported

In laboratory tests and/or small scale in-house tests no restrictions nor difficulties have been reported in any of the countries. In the Netherlands, however, the additive was treated as chemical waste after use.

Time limited large scale, realistic demonstration plants have been carried out in two countries only:

- In Germany approval was obtained for 3 projects of 2, 2 and 12 months duration, respectively.
- In Denmark it was approved to apply the additives in 3 projects with a duration of 18 months each.

In both countries it was possible to dispose of the tensid enriched after water use. In Denmark it could be led to the local sewage system under certain conditions (temperature below 35°C and low flow rate). The water was led to three step (mechanical, biological, chemical) water treatment plant, and no difficulties in this respect were reported. In Germany it was approved to dispose of the enriched water into a river after it had been treated with sodium bentonite. The bentonite separated from the water had to be treated as hazardous waste, and water led to the river had to be checked for fish toxicity, COD and BOD.

In Sweden a maximum of 50 mg/l (50ppm) is allowed in water disposed to sewers. The concentrations used in Herning and Völklingen, respectively, were approx 3 and 30 times higher than this limit.

Considerations of full-scale use, unlimited in time, are made in the Netherlands, Germany and Denmark. In Germany a concrete application for the use in a DH-network with a water volume of 78 m³ has been handed in to the authorities. No reactions have been obtained at present. In Denmark the national authorities have asked for further documentation on specific items before general permissions will be considered.

2.4.2 Level of authorities

Generally, both national, regional and local authorities are involved in the approval of additives in all countries. The local authorities will mainly be involved in matters related to the disposal, while approval for use is mostly dealt with by regional and/or national authorities.

2.4.3 Criteria

The criteria on which time-limited permissions were given in Germany and Denmark were almost equal:

- Use of heat exchangers, i.e. no direct contact to consumer installations,
- Leak indicating systems,
- Current documentation of the additives from the manufacturer,
- Documentation of the ability to decompose under anaerobic conditions,
- No introduction of tenside into surface water (Germany),
- The plants were fairly new and therefore considered safe (Denmark).

2.4.4 Demands still to be fulfilled

Subjects still to be documented in Denmark are related to which substances will be formed by decomposition of the additives and to which method to use in order to detect additives at concentrations of less than 10 µg/l.

2.4.5 Status of permission

In Germany the following projects have been approved:

- Permission for 2 months of operation with Dobon/sodiumsalicylate in a 1.2km 2* DN 4500 pipeline having a fluid volume of approximately 500 m³.
- Permission for 12 months of operation with Dobon-G/sodiumsalicylate in a system with a nominal diameter of DN 25 - DN 200 having a fluid volume of approximately 70 m³.

In Denmark:

- Permission for 18 months of operation with Habon in a 2.8 km 2 x DN 200 mm pipeline with concentration up to 1000 ppm. Optimum effect was achieved at approx. 220 ppm.
- Same with Habon-G.
- Same with Habon-G in one 7.5 km DN 125 mm pulsating pipeline + two storage tanks (in total 1000 m³. Concentration for the time being is 150 ppm. Ongoing.

2.5 Conclusion

When this survey was launched, it was clear that the level of information and the technical background was very different from country to country. This is also reflected in the answers obtained, whereby an unambiguous conclusion covering the situation in all countries cannot be drawn.

In most countries there are, however, no concrete rules related to this new technology. It seems to be clear that a certain reluctance towards the introduction of new additives in general is a common attitude. The technology has not been declined in any of the countries.

3. Appendix

3.1 Questionnaire

Survey of environmental restrictions to the use of additives for advanced fluids in district heating and cooling systems.

Please fax or mail your answers to BRUUN & SØRENSEN GROUP AS, attn.: Flemming Hammer, P.O. Box 2151, DK-8240 Risskov

Fax + 45 86 17 39 88

1. Status

ANSWERS:

1.1 Please indicate your basis on which the answers are given:

- a. General knowledge - no contact with authorities
- b. Some informal exchange of information
- c. Application under preparation
- d. Application delivered
- e. Permission with restrictions obtained
- f. Permission obtained without restrictions

e. Yes - in 3 cases!

2. Relevant additives

2.1 Which additive(s) have formally been presented to some authority with the purpose of obtaining approval for application?

Habon and Habon-G

Give product and company names and information on who to contact if relevant.

Hoechst AG, Frankfurt
Att.: Frank-Peter Lang
phone +49 69 305 7516

2.2 Please give brief description of the relevant additive(s): Type, concentration by application etc.

FRA, tenside. Habon 250 ppm
n-Alkyltrimethylammonium
n = 16

FRA, tenside. Habon-G 150 - 250 ppm
n-Alkyldimethylpolyoxethylammonium
n = 16

- 2.3 Please indicate the same information for other relevant additives, which are expected to be introduced and may already have been subject of discussion with authorities. None
- 2.4 Is the additive(s) a registered and approved chemical substance? Yes

3. Transport, storage and handling of the additive(s)

- 3.1 Give information on rules in force for transport, storage and handling. This could be in the shape of a copy of the formal rules as submitted by the manufacturer. Please refer to enclosure 1

4. Authorities

- 4.1 What type of system/activity have been considered/applied for/approved:
- plants for laboratory tests,
 - small scale in house demonstration plants
 - time limited large scale, realistic demonstration plants, c. Approval for 18 month in 3 projects.
 - full scale application without limitations of time, d. Considerations. Authorities very reluctant.
 - disposal of additive enriched water. e. Approval for disposal to sewage systems.
- 4.2 Which authority(ies) shall approve the application? Please indicate their level: National (N), Regional (R) or Local (L). Ringkøbing Country (R) backed by Danish Environmental Protection Agency (N). Local municipality shall approve of disposal.
- 4.3 Which criteria applied to the approval (if a such has been obtained)?
- The plants were fairly new and therefore considered safe.
 - Use of heat exchangers, i.e. no direct contact to consumer installations.
 - Alarm system in pipes and drainage underneath.
 - Current documentation of the additive from the manufacturer.
 - Documentation of the ability to decompose under anaerobic conditions

- 4.4 Specific demands to be expected before extended use.
- Documentation on substances formed by decomposition.
 - Description of a method of analysis with a low detection value (less than 10 µg /l).
- 4.5 Please describe formal rules in respect of district heating/cooling water (with or without advanced fluids additives) in respect to:
- a. leakages from the central station,
 - b. controlled leakages from the pipeline network,
 - c. uncontrolled leakage from the network,
 - d. leakage to consumer installations,
 - e. disposal of additive enriched water.
- 4.6 Status of permission(s) and indication of plant size.
1. Permission for 18 month of operation with Habon in 2.8 km in 2 x DN 200 mm pipeline with concentration up to 1000 ppm.
2. Same with Habon-G
3. Same with Habon-G in one 7.5 km DN 125 mm pulsating pipeline + two storage tanks (in total 1000 m³). Concentration p.t. is 150 ppm.
- Ongoing.
- 4.7 Additional remarks

Please note that you are welcome to include enclosures referring to each item.

Flemming Hammer
30 November 1994



Safety data sheet in accordance with 91/155/EEC

Trade name

Hoe S 3987

Product no.	06 FBON145	Version	4	Position	11.01.95
Substance code:	36995			Page:	1(5)

1. Identification of the substance/preparation and company

Product details

Trade name

Hoe S 3987

Supplier details:

Firm

HOECHST AG

D/65926 Frankfurt am Main

Telephone no.: 069/3050

Information provided by:

Division: D Fine chemicals and colours

Emergency telephone number: 069-305-6418

* 2. Composition/information on ingredients

Chemical characterization

Fettalkyldimethylpolyoxethylammoniumsalz
(Dobon G, 35 %ig)

UN number : 1993

Hazardous ingredients

Isopropanol

Concentration

CAS number : 67-63-0 5 %

Hazard symbols F

R phrases

11

Fatty alkyldimethylpolyoyethylammonium salt 35 %

Concentration

Hazard symbols Xi

R phrases

38

* 3. Hazards identification

Flammable.

Irritating to skin.

4. First aid measures

General information

Remove soiled or soaked clothing immediately

after contact with skin

In case of contact with skin wash off immediately with soap and water

after contact with eyes

In case of ccontact with eyes rinse thoroughly with plenty of water and seek medical advice



Safety data sheet in accordance with 91/155/EEC

Trade name

Hoe S 3987

Product no.	06 FBON145	Version	4	Position	11.01.95
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5. Fire-fighting measures

Suitable extinguishing media

water spray jet

foam

sand

carbon dioxide

dry powder

6. Accidental release measures

Methods for cleaning up/taking up

Mechanisch aufnehmen. Reste mit Wasser verdünnen and mit flüssigkeitsbindendem Material (z.B.: Sägemehl, Natriumbentonit, Universalbinder) aufnehmen.

7. Handling and storage

Handling

Advice on safe handling

Provide good ventilation when handling large quantities.

Advice on protection against fire and explosion

Traces of flammable substances can collect in the vapour space of closed systems, therefore keep sources of ignition away.

Storage

Storage class : 3A

* 8. Exposure controls/personal protection

Ingredients with occupational exposure limits to be monitored

TRGS 900 / TRGS 905

Type and origin :

MAK Maximum work place concentration

CAS number : 67-63-0

markings

2-Propanol

Limit value

400 ml/m³

Year : 1993

980 mg/m³

Extreme value limit category II,1

Personal protective equipment

General protective measures

Avoid contact with skin

Avoid contact with eyes

Hand protection

: Gloves



Safety data sheet in accordance with 91/155/EEC

Trade name

Hoe S 3987

Product no.	06 FBON145	Version	4	Position	11.01.95
Substance code:	36995			Page:	3 (5)

* 9. Physical and chemical properties

Appearance

Form : Pasty
 Colour : beige
 Odour : of isopropanol

Date relevant to safety

Changes in physical state

Pourpoint

Method : DIN/ISO 3016 approx. 18 °C

Flash point

Method : DIN 51755 36 °C

Density

Method : DIN 51757 at 60 °C 0.98 g/cm³

Solubility in water

soluble, turbid at 15 °C 0.5 g/l

pH value

6 to 7
 (at 10 g/l H₂O)
 at 20 °C

Combustion number : BZ1

Does not catch fire

10. Stability and reactivity

11. Toxicological information

Acute oral toxicity (LD₅₀)

> 2000 mg/kg

Species : rat
 Method : OECD 401

Irritant effect on skin

irritant
 Species : rabbit
 Method : OECD 404



Safety data sheet in accordance with 91/155/EEC

Trade name

Hoe S 3987

Product no.	06 FBON145	Version	4	Position	11.01.95
Substance code:	36995			Page:	4 (5)

Irritant effect on eyes

non-irritant

Species : rabbit eye

Method : OECD 405

12. Ecological information

Data on elimination (persistence and degradability) :

Biodegradability

> 90 %

Method : OECD confirmatory test

Ecotoxic effect

Fish toxicity (LC₅₀)

8.5 mg/l

Duration of exposure

96 h

Species : zebra fish

Method : OECD 203

Bacteria toxicity (EC₅₀)

> 1000 mg/l

Method : OECD 209

13. Disposal considerations

Product

In accordance with local authority regulations, take to special waste incineration plant

* 14. Transport information

Road transport

ADR 3/31C

GGVS 3/31C

RID 3/31C

GGVE 3/31C

Product characteristic

ENTZUENDBARER FLUESSIGER STOFF, N.A.G. (ISOPROPANOL (ISOPRPYLA LKOHOL))

Hazard no. 30

Substance number 1993

Inland waterways transport

ADNR 3/31C

Product characteristic



Safety data sheet in accordance with 91/155/EEC

Trade name

Hoe S 3987

Product no.	06 FBON145	Version	4	Position	11.01.95
Substance code:	36995			Page:	5 (5)

Marine transport

IMDG-Code	3.3/1993/III		
EmS	3-07 *	MFAG	305

Correct technical name

FLAMMABLE LIQUID, N.O.S. (ISOPROPYL ALCOHOL)

Air transport

ICAO / IATA-DGR	3/1993/III
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Correct technical name

FLAMMABLE LIQUID, N.O.S. (ISOPROPYL ALCOHOL)

Further information

Dispatch by post	Not permitted.
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* 15. Regulatory information

Labelling in accordance with GefStoffV/EC
hazard warning labelling compulsory

Hazard symbols	Xi Irritant
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Hazardous component (s) to be indicated on label

contains	Isopropanol
	Fatty alkyldimethylpolyoxethylammonium salt

R phrases

10	Flammable.
38	Irritating to skin.

S phrases

16	Keep away from sources of ignition --- No smoking.
26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
28.2	After contact with skin, wash immediately with water and soap.
37/39	Wear suitable gloves and eye/face protection.

National regulations :

Water Hazard Class (Germany) : 1 (self-classification)

16. Other information

This information is based on our present state of knowledge. It should not therefore be construed as guaranteeing specific properties of the products described or their suitability for a particular application.

Chapter which has been changed in respect of its previous version is marked with ' * '.

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