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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : B01D 19/04, D21H 21/12

A1

(11) International Publication Number: **WO 00/50147**

(43) International Publication Date: 31 August 2000 (31.08.00)

(21) International Application Number: PCT/US00/03975

(22) International Filing Date: 17 February 2000 (17.02.00)

(30) Priority Data:
09/256,059 24 February 1999 (24.02.99) US

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(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: HYDROCARBON OIL FREE DEFOAMER

(57) Abstract

The present invention is directed to foam control compositions and their use in aqueous systems. The foam control compositions are particularly useful in the processing of pulp and paper and the treatment of effluent water.

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HYDROCARBON OIL FREE DEFOAMER

FIELD OF THE INVENTION

The present invention relates to foam control compositions, their preparation and use in aqueous systems. The foam control compositions are particularly useful in the processing of pulp and paper and the treatment of effluent water.

BACKGROUND OF THE INVENTION

Foam can present serious problems in the manufacture of pulp and paper. Lack of adequate foam control in the paper slurry can limit or halt production, as well as affect finished product quality.

Defoamers, when added to a foaming liquid, can prevent bubble formation or cause coalescence of smaller bubbles into larger ones, leading to rupture. Most conventional defoamers include a hydrophobic material having a melting point greater than 40° C, such as a diamide and/or a hydrophobically modified insoluble particle, e.g., silica, dispersed in a hydrocarbon oil phase. Many of these compositions also

contain silicone oil. A problem with these types of compositions is that they quickly become unstable, and a settling of individual components, such as silica, occurs. Hydrophobic materials with melting points above 40° C will precipitate rapidly after the processing temperatures fall below their melting point when dispersed in a hydrocarbon oil phase. Pure organic-based defoamers are not highly effective and require large amounts of material to defoam systems, while silica-based defoamers are expensive because large amounts of the silica particles are required to perform effectively.

DETAILED DESCRIPTION OF THE INVENTION

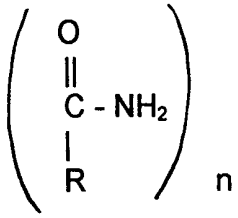
The present invention relates to a water-based defoaming agent containing (1) an ester of a dicarboxylic acid and a monohydric alcohol, (2) at least one predominantly hydrophobic material having a melting point greater than 40° C selected from the group consisting of hydrocarbon waxes, fatty amides, fatty acids and fatty alcohols, (3) a surfactant selected from the group consisting of polyethylene glycol esters, sorbitan/sorbitol esters, ethoxylated fatty alcohols, fatty acids and fatty ethers, and (4) water. In a preferred embodiment, the defoaming agent further includes a polyether modified silicone copolymer, an aqueous polyacrylate and an alkali material.

The present invention provides a defoaming agent with improved efficacy in aqueous systems that is particularly effective at controlling foam in the paper making process. The present invention provides a water-based defoamer composition with improved stability and no particle precipitation over a temperature range of about 10° C to 50° C. Furthermore, the invention provides an "environmentally friendly"

defoamer composition comprising low or no volatile organic carbon (VOC) content and no dioxin precursor containing hydrocarbon oils.

The dicarboxylic acid ester is formed from the reaction of a dicarboxylic acid with a monohydric alcohol. The dicarboxylic acid is selected from the group consisting of adipic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid and isomers thereof. These acids are then reacted with alcohols selected from the group consisting of hexyl, octyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl alcohol, and isomers thereof.

The hydrophobic material with a melting point greater than 40° C includes fatty acid amides with the general formula:



wherein n is an integer from 2 to 6, and R is a saturated or unsaturated, straight or branched aliphatic group having from 5 to 22 carbons.

The fatty amides are formed from the reaction of polyamine containing at least one alkylene group having from 2 to 6 carbon atoms and a fatty acid having from 5 to 22 carbon atoms not including the carboxyl group carbon. Examples of suitable hydrophobic amides formed from this reaction include but are not limited to methylene bis acrylamide, methylene bis lauramide, ethylene bis stearamide, ethylene bis behenamide, and ethylene bis oleoamide. The aliphatic fatty alcohols

and fatty acids are saturated, linear or branched and contain at least 12 carbon atoms, while the hydrocarbon wax has a melting point of from about 40° C to 120° C.

The emulsifying surfactants are preferably nonionic surfactants and include polyethylene glycol esters such as PEG 400 dioleate and PEG 600 dioleate, sorbitan/sorbital esters such as sorbitan monooleate, POE (20) sorbitan monooleate and POE (40) sorbitol hexaoleate, ethoxylated fatty acids, ethoxylated fatty alcohols, and ethoxylated fatty ethers such as POE (40) stearate, POE (20) stearyl alcohol and POE (10) oleyl ether. The polyether-modified silicone copolymer is a silicone copolymer modified with ethylene oxide and propylene oxide which results in a copolymer with a cloud point of from about 40° C to less than about 25° C, and a molecular weight range of from about 10,000 to 40,000.

The polyacrylates that are encompassed by the present invention are aqueous, acidic, acrylic emulsion copolymers that thicken by an uncoiling action of the polymer chain upon neutralization with an alkali material. The preferred polyacrylate is a copolymer of ethylacrylate and methacrylic acid. The alkali material can be sodium hydroxide, potassium hydroxide, ammonium hydroxide, or triethanolamine.

In a preferred embodiment, the present invention relates to the use of a dicarboxylic acid ester, without organic solvent or hydrocarbon oil, as a carrier for the high melting point hydrophobic material and a surfactant selected from the group consisting of polyethylene glycol esters, sorbitol/sorbitan esters, ethoxylated fatty acids, ethoxylated fatty alcohols and ethoxylated fatty ethers, emulsified in water to form a stable

dispersion of particles that does not precipitate upon cooling below the melting point of the hydrophobic material. The dispersions are stable at temperatures of from about 10° C to 50° C for about 6 weeks.

Preferred amounts of the components of the defoamer composition of the present invention are as follows:

(Values in percent by weight)

Component	Preferred %	Particularly Preferred %
Dicarboxylic Acid Ester	5 - 60	10 - 40
Hydrophobic material	0.5 - 20	1 - 10
Surfactants	0.5 - 30	5 - 20
Modified silicone copolymer	0.1 - 5	0.1 - 5
Water	40 - 95	40 - 80
Polyacrylate	0.5 - 5	0.5 - 5
Alkali material	0.1 - 5	0.5 - 5

The defoamers are prepared by charging all the material excluding the water to a vessel, heating to about 120° C, and holding at this temperature for about 30 minutes. The mixture is added to a vessel that has been charged with the water phase maintained under constant agitation. The dispersion is then cooled to below 45° C, at which time the polyacrylate is added and then neutralized with the alkali material.

In the testing of the present invention, various defoamers were tested in a recirculation test cell. The foaming medium is circulated from the bottom of a calibrated graduated column via a pump and returned

down through the top of the column. This action agitates the medium and causes foam which flows up the calibrated tube and allows determination of foam height at different time intervals. The calibrated column is wrapped with heat tape and kept at a constant temperature (+/-2° F) via a probe and temperature controller. The foam test cell holds approximately 1200 ml of medium. The column is filled with medium and recirculated briefly to evacuate all the air from the loop.

Examples

The defoamers noted below were tested using the synthetic medium at a temperature of 130° F and a pH of 7.5. The conductivity of the medium was 2400 umhos. Control time was 6.5 seconds to top.

Example 1 (Numbers below correspond to entries in Figure 1)

1) An emulsion antifoam containing hydrocarbon oil, ethylene bis stearamide, surfactants and water.

2) An emulsion antifoam of the present invention containing diisononyl adipate, wax, surfactants, silicon copolymer, ethylene bis stearamide, polyacrylate, water and sodium hydroxide.

3) An emulsion antifoam of the present invention containing dioctyl sebacate, ethylene bis stearamide, wax, surfactants, silicone copolymer, polyacrylate, water, and sodium hydroxide.

4) An emulsion antifoam of the present invention containing diisoctyl phthalate, ethylene bis stearamide, surfactants, and water.

5) An emulsion antifoam of the present invention containing diisononyl adipate, ethylene bis stearamide, surfactants, and water.

As shown in Figure 1, an amide particulate antifoam emulsion containing hydrocarbon oil (No. 1) is not as effective as the other examples which are variations of the present invention and contain various dicarboxylic acid esters. All formulations were run at a dosage of 10 ul.

Example 2 (Numbers below correspond to entries in Figure 2)

The defoamers listed below were tested using the synthetic medium at a temperature of 125° F and a pH of 7.0. The conductivity of the medium was 4600 umhos. Control time was 8 seconds to top.

6) An emulsion antifoam containing hydrocarbon oil, ethylene bis stearamide, surfactants and water.

7) An emulsion antifoam of the present invention containing diisononyl adipate, ethylene bis stearamide, surfactants, and water.

8) An emulsion antifoam of the present invention containing diisoctyl phthalate, ethylene bis stearamide, surfactants, and water.

9) An antifoam from U.S. Patent 3,959,175 containing polybutene and ethylene bis stearamide.

10) An emulsion antifoam of the present invention containing diisononyl adipate, wax, surfactants, silicon copolymer, ethylene bis stearamide, polyacrylate, water and sodium hydroxide.

As shown in Figure 2, tests 7, 8 and 10 provide superior performance when compared to the hydrocarbon oil/amide emulsion and the polybutene/amide based product. All products were tested at a dosage of 12 ul.

While this invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications of this invention will be obvious to those skilled in the art. The appended claims and this invention generally should be construed to cover all such obvious forms and modifications which are within the true spirit and scope of the present invention.

We claim:

1. A water-based defoaming agent composition comprising:

(a) an ester of dicarboxylic acid and a monohydric alcohol;

(b) a hydrophobic material having a melting point greater than 40° C selected from the group consisting of hydrocarbon waxes, fatty amides, fatty acids and fatty alcohols; and

(c) a surfactant selected from the group consisting of polyethylene glycol esters, sorbitan/sorbitol esters, ethoxylated fatty alcohols, fatty acids and fatty ethers.

2. The composition as recited in claim 1 further comprising a polyether modified silicone copolymer.

3. The composition as recited in claim 1 further comprising an aqueous polyacrylate.

4. The composition as recited in claim 1 wherein said defoaming agent forms a stable dispersion at from about 10° - 50° C.

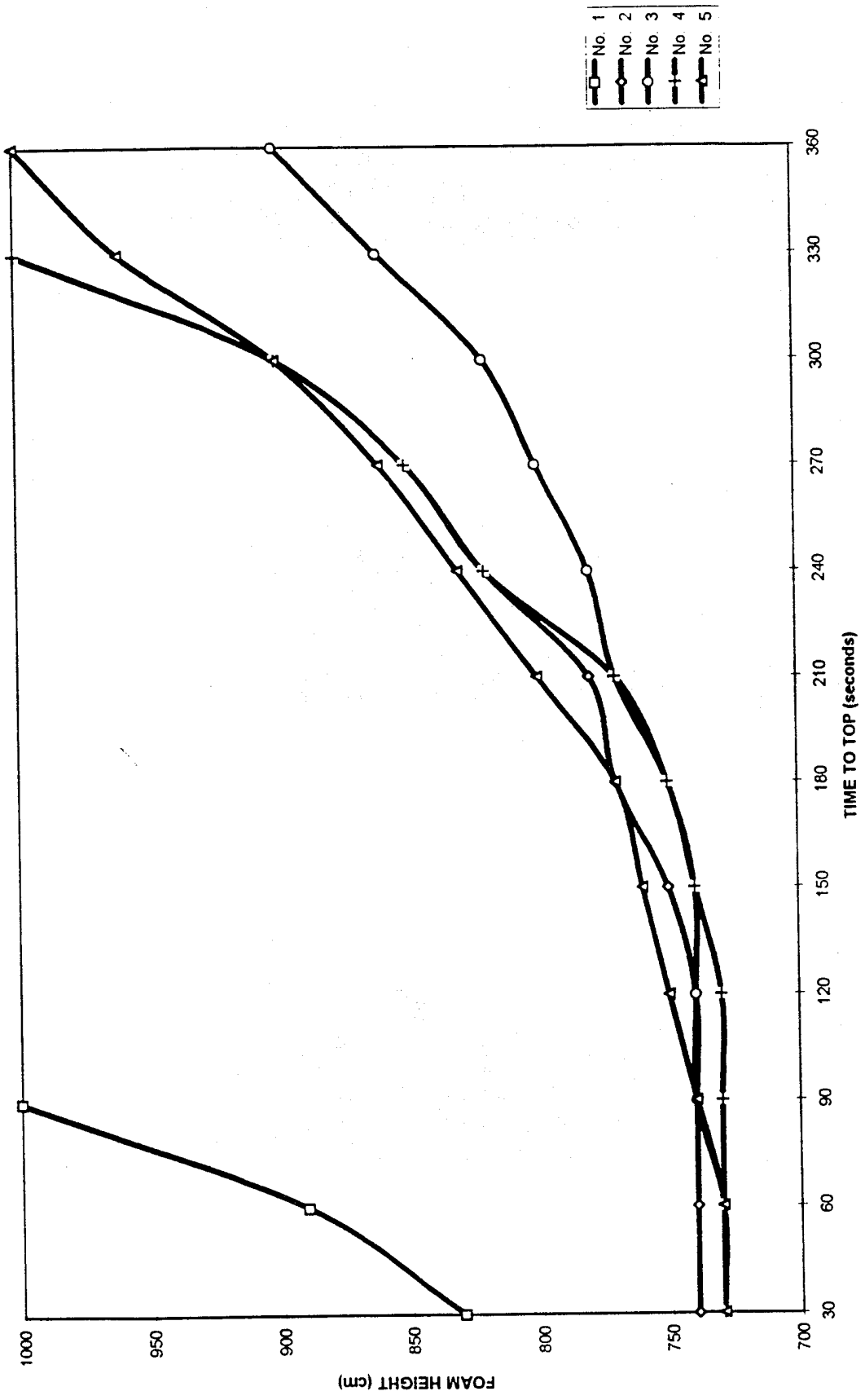
5. The composition as recited in claim 1 wherein said ester is a diisononyl adipate.

6. The composition as recited in claim 1 wherein said ester is a dioctyl sebacate.

7. The composition as recited in claim 1 wherein said ester is a diisooctyl phthalate.

8. The composition as recited in claim 1 wherein said amide is ethylene bis stearamide.

FIGURE 1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No. 3
No. 4
No. 5
FOAM HEIGHT (cm)
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950
900
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750
700
TIME TO TOP (seconds)
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60
90
120
150
180
210
240
270
300
330
360

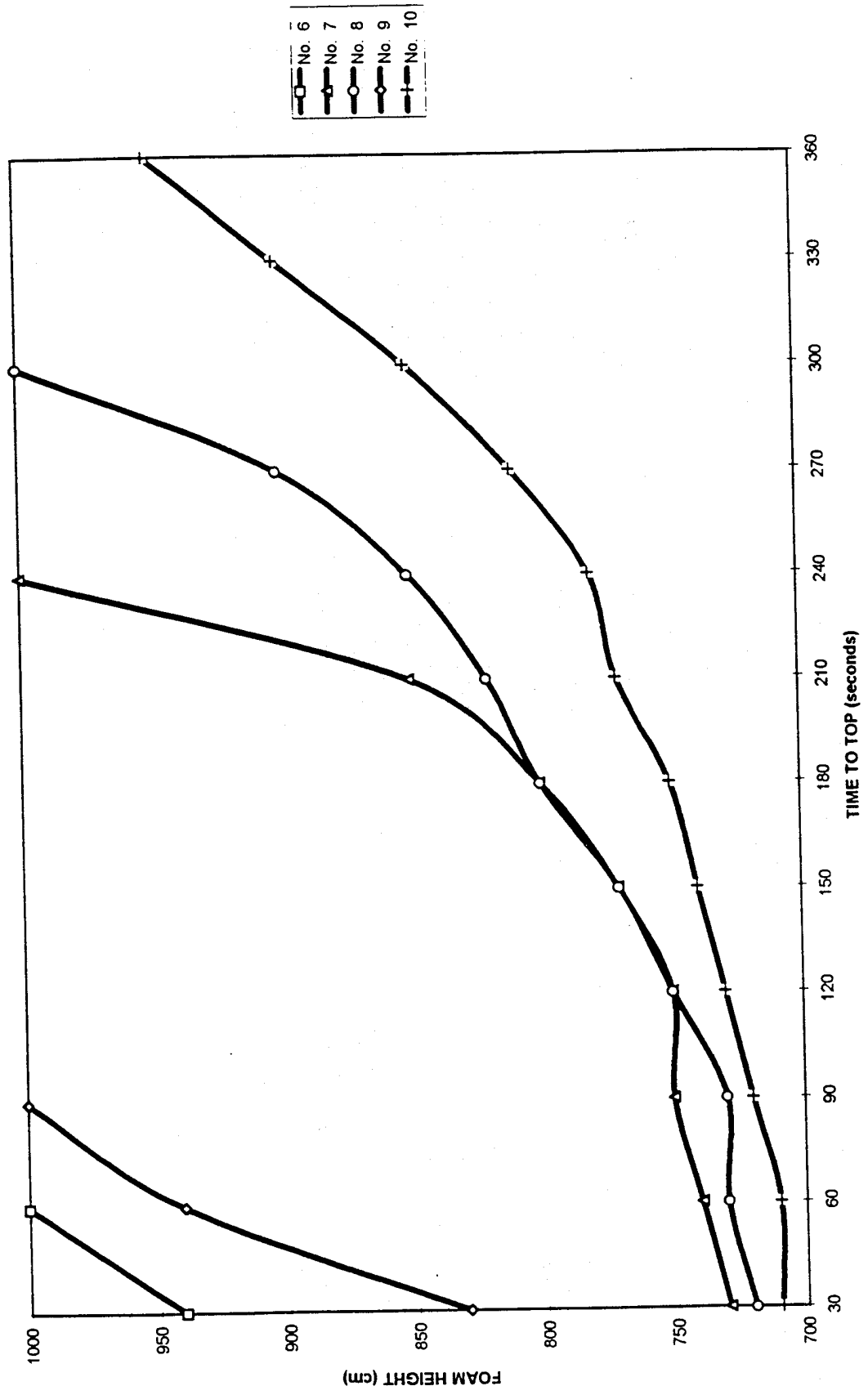
No. 6
No. 7
No. 8
No. 9
No. 10
FOAM HEIGHT (cm)
1000
950
900
850
800
750
700
TIME TO TOP (seconds)
30
60
90
120
150
180
210
240
270
300
330
360

FIGURE 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/03975

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D19/04 D21H21/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01D D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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WPI Data, EPO-Internal, PAJ

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[X] Further documents are listed in the continuation of box C.

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2

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