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(54) **Title:** GAS BARRIER COATING COMPOSITION FOR PAPER AND FILMS

(57) **Abstract:** The invention is directed to a coating composition comprising – 1 - 10 weight % polyvinyl alcohol (PVOH) or vinylacetate/ethylene/vinyl alcohol terpolymer (EVOH), – 0,01 to 5 weight% of an alcohol having 5 to 30 carbon atoms, – 10 – 90 weight % water. The coting composition can be used as gas barrier on paper and films and/or for food packaging.

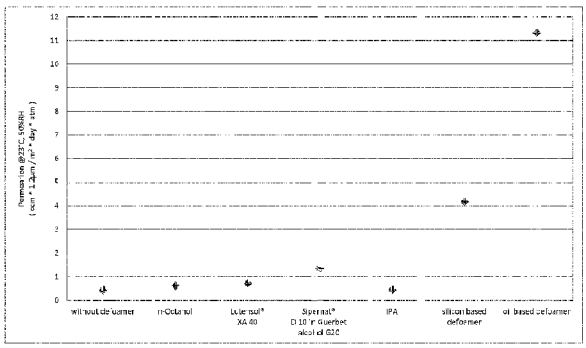

Fig. 1

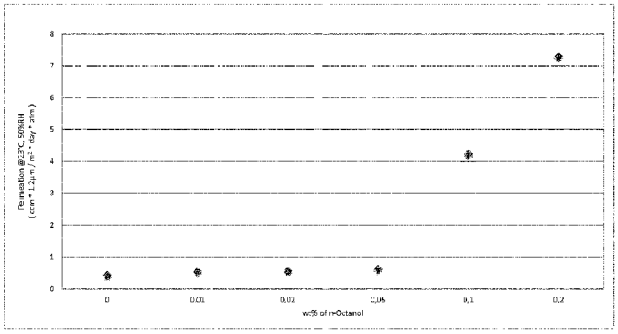

Fig. 2

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Gas barrier coating composition for paper and films

The invention is directed to a coating composition to improve the gas barrier of paper and films.

Background

For packaging purposes, it is known to provide paper or card box with gas barrier properties (OTR properties), i.e. by coating or impregnating with certain polymers. Besides using environmental critically fluorinated or chlorinated polymers, polyvinyl alcohol (PVOH) or vinylacetate/ethylene/vinyl alcohol (EVOH) are known as coating material for this purpose.

In praxis, aqueous solutions or suspensions of PVOH or EVOH are prepared, supplemented with further additives, coated on the paper and then dried. Although this method is quite straightforward, it suffers from the very prominent foaming behavior of these polymers. Foams originating form PVOH and EVOH are quite stable and are an obstacle for the production steps. In order to reduce the foaming, so called anti-foaming agents can be added, but these compounds (usually oils and/or surfactants) impart the gas barrier properties due to their chemical nature.

For example, the main drawback of classical oil based defoamers to be used with PVOH is their tendency to reduce the barrier properties because of their tendency to form pinholes upon drying.

Solvent based defoamers like isopropyl alcohol and the like show significantly lower defoaming performance that necessitate the use of large quantity of these to achieve satisfactory defoaming ability. Such low alcohol based defoamers cannot be used in the paper industry because of the volatile organic content problematic.

In this respect, US20140377486A1 discloses the use of so called Guerbet alcohol alkoxylates having the chemical formula $RO(CH_2CH_2O)_x$ with R= $C_{13}H_{21}$ and X at least 8. Similar, US2016083606 describes the use of Tergitol TMN6 having the chemical formula $(C_4H_9)_2$ CH $(OCH_2CH_2)X$ with X=8.

It was an object of the invention to provide a coating composition for paper comprising PVOH or EVOH having a good gas barrier but simultaneously a reduced foaming behavior without using traditional anti-foaming agents.

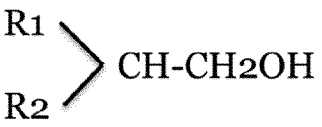
Surprisingly it was found that the addition of alcohols having a certain chain length in low concentration to coating compositions comprising PVOH or EVOH are suitable to reduce foaming without impairing gas barrier properties.

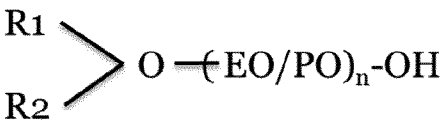
Object of the invention was a coating composition comprising

- 1 - 10 weight % polyvinyl alcohol (PVOH) or vinylacetate/ethylene/vinyl alcohol terpolymer (EVOH)
- 0,01 to 5 weight% of an alcohol
- 10 – 90 weight % water

characterized in that the alcohol is a Guerbet alcohol and/or Guerbet alcohol alkoxylate according to the formula (I) $RO(CH_2CH_2O)_xH$
with R= H or an aliphatic residue with 6 to 12 carbon atoms and X= 2-6

The alcohols used may be cyclic, branched or non-branched and can be provided with one or up to 5 hydroxy groups at any position of the chain. However, in praxis the use of so called Guerbet alcohols and Guerbet alcohol alkoxylates are especially advantageously. Guerbet alcohols as used in the present invention are obtained by Guerbet reaction of two small chain alcohols. Suitable Guerbet alcohols and Guerbet alcohol alkoxylates are for example :





wherein R1 = linear or branched, substituted or unsubstituted, saturated or unsaturated C2-12 alkyl; wherein R2 = linear or branched, substituted or unsubstituted, saturated or unsaturated C2-12 alkyl; wherein EO/PO are alkoxy moieties selected from ethoxy, propoxy, or mixtures thereof; wherein n is the average degree of alkoxylation and is in the range of from 2 to 10.

Preferable, the aliphatic residue is $C_{10}H_{21}$ and X = 4 - 8.

Preferable, the polyvinyl alcohol (PVOH) used in the coating composition has a degree of hydrolysis between 70% to 99,9%, more preferable 90 – 99 % and/or has a degree of polymerization between 200 and 4500, more preferable 300 – 2000.

Preferable, the vinylacetate/ethylene/vinyl alcohol terpolymer (EVOH) used in the coating composition has a degree of hydrolysis between 80% and 99,9% and/or a degree of polymerization between 200 and 4500 and/or an ethylene content of 1 – 20 Mol%.

The coating composition contains preferably no silicon compound, i.e. in absence of a silicon compound.

In a variant of the invention, the coating composition contains 0,025 to 0,05 weight% of silica, preferable a hydrophobized silica. Suitable silicas are for example Sipernat® D 10 or Aerosil, commercialized by Evonik. In this variant, the addition of hydrophobic compounds like paraffin and/or alcohols having 8 – 30 carbon atoms, especially the above defined Guerbet alcohols and Guerbet alcohol alkoxylates are preferred.

The coating composition according to the invention has preferably an oxygen transmission rate (OTR) at 23°C and 50% relative humidity lower than 1cc/m^2.day for 1gsm (g/m^2) coat weight. The OTR of the coating composition of the invention is measured using PET film rather than paper for better evaluation. PET film has only moderate gas barrier properties, therefore the measured OTR originates from the coating composition.

The coating composition according to the invention is preferable prepared before being applied to a substrate as optically homogeneous solution i.e. as mixture and/or suspension. This is achieved by using the alcohols as defined at low concentrations.

The coating composition can be used as gas barrier and/or as oil/fat barrier on substrates like paper, card box or any cellulose-based material and films (Packaging films, like PE, PP, PET), especially for food packaging.

Examples

“Lutensol® XA 40” is a compound available from BASF with R=$C_{10}H_{21}$ and X=4

“Guerbet alcohol G20” is a compound with R=H and X=10

EXAMPLE 1

A laboratory evaluation of six defoamers was conducted using perforated disc beating method (DIN EN 12728). PVOH/EVOH and defoamer were prepared in an aqueous solution. The coating composition is then coated on PET substrate film for oxygen transmission rate (OTR) measurement. The barrier layer film was analyzed by MOCON OX-TRAN® Model 2/21 Series and is shown in Fig 1 as "Gas Permeation rate of EXCEVAL™ AQ-4104 with 0.05 wt% different defoamers". The data in TABLE 1 and Fig. 1 clearly indicates that the defoamer of the present invention, i.e., n-Octanol, Lutensol® XA 40 and Sipernat® D 10 in Guerbet alcohol blend, works effectively as an defoamer agent and also has a good barrier when the defoamers are compatible with PVOH/EVOH.

Comparative Example 1

The procedure of EXAMPLE 1 was repeated, but using conventional defoamers, i.e. IPA, silicon based and oil based defoamers. The results show that if the coating composition is turbid, the defoamer has good defoaming performance, however, very bad barrier property due to the immiscibility in PVOH/EVOH solution.

	without defoamer	n-Octanol	Lutensol® XA 40	Sipernat® D 10 in Guerbet alcohol G20	IPA	Silicon based defoamer	Oil based defoamer
Clarity*	+	+	+	+	+	–	–
ΔV@0min	69	20	29	11	54	5	6
ΔV@1min	58	12	2	2	49	1	1
ΔV@5min	52	10	1	1	45	1	1

* clarity is defined by optical observation. + : clear solution. – : turbid solution.

TABLE 1 (Defoaming test of EXCEVAL™ AQ-4104 with 0.01wt % different defoamers)

EXAMPLE 2

A laboratory evaluation of five different alcohols was conducted using perforated disc beating method (DIN EN 12728). PVOH/EVOH and defoamer were prepared in an aqueous solution. The coating composition is then coated on PET substrate film for oxygen transmission rate (OTR) measurement. The barrier layer film was analyzed by MOCON OX-TRAN® Model 2/21 Series and is shown in Fig 2 as "Gas Permeation rate of EXCEVAL™ AQ-4104 with different wt% of n-Octanol". The data in TABLE2 shows that shorter carbon chain alcohol has better compatibility with aqueous solution, but longer carbon chain alcohol has better defoaming performance. It means that more hydrophobic alcohol as defoamer can significantly reduce foam formation. The miscibility in water is slightly increased, when n-Octanol is mixed with IPA, but the defoaming effectiveness is decreased. It responds again that influence of miscibility on defoaming effect. Table 3 and Fig. 2 show also clearly that more n-Octanol in PVOH solution has less compatibility but higher gas permeation rate(worse barrier property); however, better defoaming efficiency. It concludes that, to having a good barrier is essential to have a homogeneous/qusi-homogeneous solution, but at the same time, the defoamer has a good defoaming performance.

	without defoamer	IPA	n-Butanol	Iso-Butanol	n-Octanol/IPA (1/9)	n-Octanol
Clarity*	+	+	+	+	+	⊗
ΔV@0min	69	59	52	54	22	4
ΔV@1min	58	44	40	43	18	2
ΔV@5min	52	40	34	40	16	1

* clarity is defined by optical observation. + : clear solution. ⊗ : oil spots on surface.

TABLE 2 (Defoaming test of EXCEVAL™ AQ-4104 with 0.05wt % different alcohols)

	0	0.01	0.02	0.03	0.04	0.05	0.1	0.2
Clarity*	+	+	⊗	⊗	⊗	⊗	–	–
ΔV@0min	69	20	4	4	4	4	4	4
ΔV@1min	58	12	2	2	2	2	3	2
ΔV@5min	52	10	1	1	1	1	2	1

* clarity is defined by optical observation. + : clear solution. ⊗ : oil spots on surface. – : turbid solution.

TABLE 3 (Defoaming test of EXCEVAL™ AQ-4104 with different wt% of n-Octanol)

EXAMPLE 3

The procedure of EXAMPLE 2 was repeated, but using different silica/Guerbet alcohol mixture as defoamers. There are four different hydrophobicity silica utilized, among them Sipernat® D 10 and Aerosil® R 202 are very hydrophobic, Aerosil® R 805 is hydrophobic and Aerosil® R 816 is semi-hydrophobic. The results from TABLE 4 indicates also more hydrophobic silica/Guerbet alcohol mixture has significantly better defoaming performance.

	without defoamer	Sipernat® D 10 in Guerbet alcohol G20	Aerosil® R 805 in Guerbet alcohol G20	Aerosil® R 202 in Guerbet alcohol G20	Aerosil® R 816 in Guerbet alcohol G20
Clarity*	+	⊗	⊗	⊗	⊗
ΔV@0min	83	22	20	26	73
ΔV@1min	70	3	3	3	65
ΔV@5min	63	1	1	2	62

* clarity is defined by optical observation. + : clear solution. ⊗ : oil spots on surface.

TABLE 4 (Defoaming test of KURARAY POVAL™ 4-88 with 0,01wt% defoamers containing 2.5 wt% different nano-silica)

EXAMPLE 4

The procedure of EXAMPLE 1 was repeated, but defoaming test was processed at 50°C. The data in TABLE 5 show similar defoaming performance as at room temperature (EXAMPLE 1).

	Oil based defoamer	Lutensol® XA 40	n-Octanol	IPA
Clarity*	–	+	+	+
ΔV@0min	8	16	29	50
ΔV@1min	2	2	19	28
ΔV@5min	1	1	5	14

* clarity is defined by optical observation. + : clear solution. – : turbid solution.

TABLE 5 (Defoaming test at 50°C of EXCEVAL™ AQ-4104 with 0.01wt% different defoamers)

Claims

1) Coating composition comprising
   - 1 - 10 weight % polyvinyl alcohol (PVOH) or vinylacetate/ethylene/vinyl alcohol terpolymer (EVOH)
   - 0,01 to 5 weight% of an alcohol
   - 10 – 90 weight % water

   characterized in that the alcohol is a Guerbet alcohol and/or Guerbet alcohol alkoxylate according to the formula (I) $RO(CH_2CH_2O)_xH$
   with R= H or an aliphatic residue with 6 to 12 carbon atoms and X= 2-6

2) Coating composition according to claim 1 characterized in the absence of a silicon compound.

3) Coating composition according to claim 1 characterized by comprising 0,025 to 0,05 weight% of silica.

4) Coating composition according to claim 1 characterized by comprising 0,025 to 0,05 weight% of hydrophobized silica.

5) Coating composition according to any of the claims 1 to 4 characterized in that the polyvinyl alcohol (PVOH) has a degree of hydrolysis between 70% to 99,9%.

6) Coating composition according to any of the claims 1 to 4 characterized in that the polyvinyl alcohol (PVOH) has a degree of polymerization between 200 and 4500.

7) Coating composition according to any of the claims 1 to 4 characterized in that the vinylacetate/ethylene/vinyl alcohol terpolymer (EVOH) has a degree of hydrolysis between 80% and 99,9%.

8) Coating composition according to any of the claims 1 to 4 characterized in that the vinylacetate/ethylene/vinyl alcohol terpolymer (EVOH) has a degree of polymerization between 200 and 4500.

9) Coating composition according to any of the claims 1 to 4 characterized in that the vinylacetate/ethylene/vinyl alcohol terpolymer (EVOH) has an ethylene content of 1 – 20 Mol%.

10) Coating composition according to any of the claims 1 to 9 characterized in that the coating composition has an the oxygen transmission rate at 23°C and 50% relative humidity is lower than 1cc/m^2.day for 1gsm (g/m^2) coat weight on PET film.

11) Use of the coating composition according to claims 1 to 10 as gas barrier and/or as oil/fat barrier on paper and films.

12) Use of the coating composition according to claims 1 to 10 as gas barrier and/or as oil/fat barrier for food packaging.

Drawings

Fig. 1

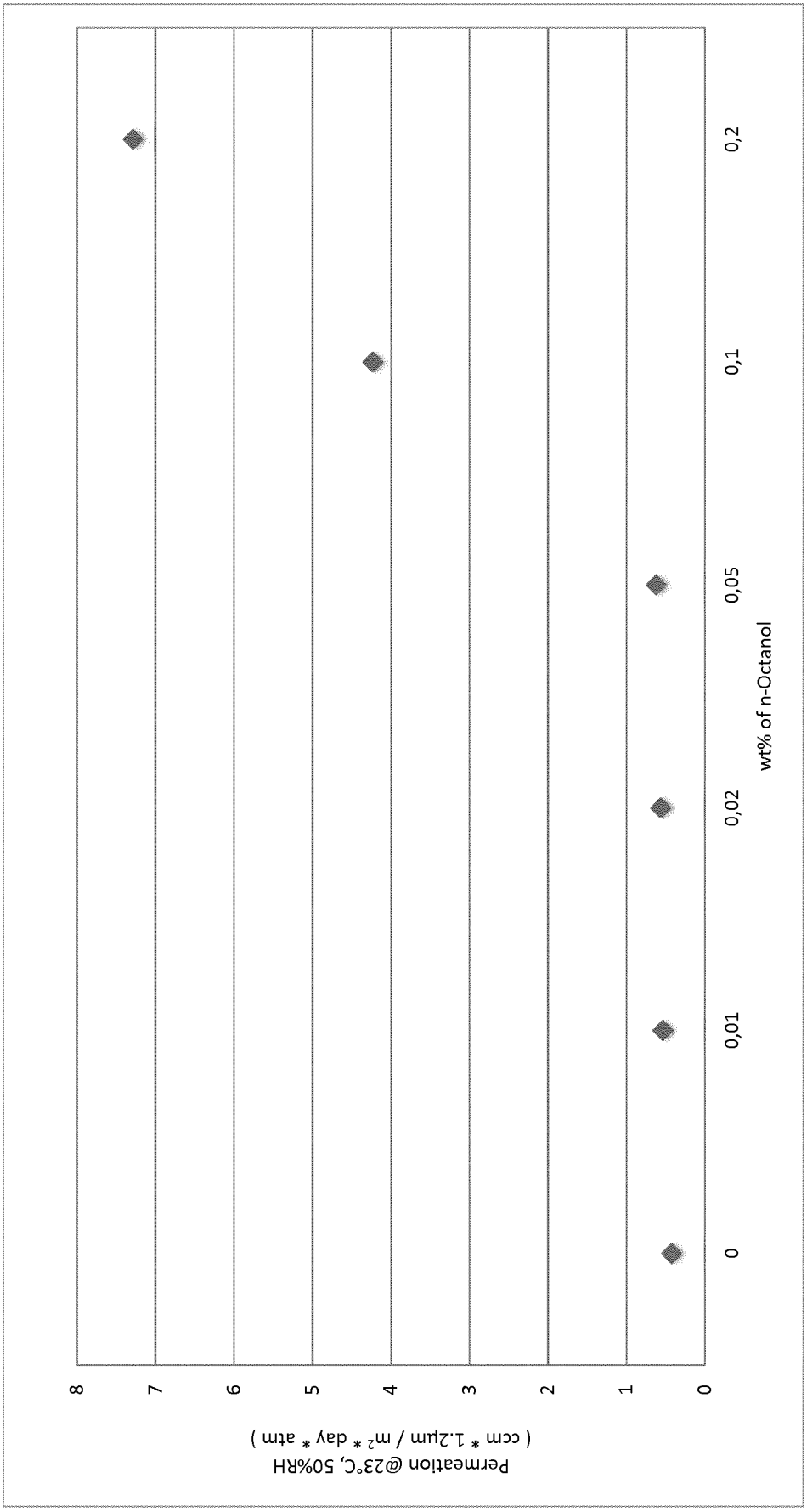

Permeation @23°C, 50%RH
(ccm * 1.2µm / m² * day * atm)
0
1
2
3
4
5
6
7
8
0
0,01
0,02
0,05
0,1
0,2
wt% of n-Octanol

Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/070894

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D129/04
ADD.

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)
C09D C08K

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
31 August 2018	07/09/2018

Name and mailing address of the ISA/	Authorized officer
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	US 2016/024326 A1 (KHAN ASAD [GB] ET AL) 28 January 2016 (2016-01-28) coating 7B; table 13	7-9

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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