

663955  
AUSTRALIA

SPRUSON & FERGUSON

PATENTS ACT 1990

**PATENT REQUEST: STANDARD PATENT**

I/We, the Applicant(s)/Nominated Person(s) specified below, request I/We be granted a patent for the invention disclosed in the accompanying standard complete specification.

**[70,71] Applicant(s)/Nominated Person(s):**

Kimberly-Clark Corporation, of 401 North Lake Street, Neenah,  
Wisconsin, 54956, UNITED STATES OF AMERICA

**[54] Invention Title:**

Preserved Polysiloxane Emulsions for Treating Tissues

**[72] Inventor(s):**

Rae Ellen Syverson, Wendell Eugene Landin and Rebecca Suzanne  
Walter

**[74] Address for service in Australia:**

Spruson & Ferguson, Patent Attorneys  
Level 33 St Martins Tower  
31 Market Street  
Sydney New South Wales Australia (Code SF)

**Details of Basic Application(s):**

**[31] Appl'n No(s):**

904,796

**[33] Country:**

US

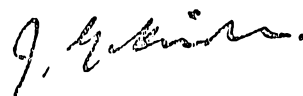
**[32] Application Date:**

26 June 1992

DATED this SIXTEENTH day of JUNE 1993

Kimberly-Clark Corporation

By:



Registered Patent Attorney

IRN: 237864

INSTR CODE: 56610

S 038301

160693

Australia

Patents Act 1990

NOTICE OF ENTITLEMENT

I, Martin Herman Michael,  
of Kimberly-Clark Corporation, with offices at 401 North Lake Street,  
Neenah, Wisconsin 54957-0349, U.S.A.

being authorised by the Applicant(s)/Nominated Person(s) in respect of  
an application entitled:

PRESERVED POLYSILOXANE EMULSIONS FOR TREATING TISSUES

state the following:

1. The Applicant(s)/Nominated Person(s) has/have, for the following reasons, gained entitlement from the actual inventor(s):


The Applicant/Nominated Person is the assignee of the actual inventor(s).

2. The Applicant(s)/Nominated Person(s) is/are entitled to rely on the basic application(s) listed on the Patent Request as follows:

The Applicant(s)/Nominated Person(s) is the assignee of the basic applicant(s).

3. The basic application(s) listed on the Patent Request is/are the application(s) first made in a Convention Country in respect of the invention.

DATED this 6th day of January, 1993.

  
(Signature)

Martin Herman Michael  
Vice President and Chief Counsel  
(Name & Title)



AU9341296

**(12) PATENT ABRIDGMENT (11) Document No. AU-B-41296/93**  
**(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 663955**

- (54) Title  
**PRESERVED POLYSILOXANE EMULSIONS FOR TREATING TISSUES**
- International Patent Classification(s)  
(51)<sup>5</sup> **C08K 005/10 C08L 083/04**
- (21) Application No. : **41296/93** (22) Application Date : **16.06.93**
- (30) Priority Data
- (31) Number (32) Date (33) Country  
**904796 26.06.92 US UNITED STATES OF AMERICA**
- (43) Publication Date : **06.01.94**
- (44) Publication Date of Accepted Application : **26.10.95**
- (71) Applicant(s)  
**KIMBERLY-CLARK CORPORATION**
- (72) Inventor(s)  
**RAE ELLEN SYVERSON; WENDELL EUGENE LANDIN; REBECCA SUZANNE WALTER**
- (74) Attorney or Agent  
**SPRUSON & FERGUSON , GPO Box 3898, SYDNEY NSW 2001**
- (56) Prior Art Documents  
**US 5084270**  
**US 4797272**  
**US 4368189**
- (57) Claim

1. An aqueous polysiloxane emulsion having a pH of from 6.5 to 8, at least 0.1 weight percent ethylenediaminetetraacetic acid, and 0.1 to 1 weight percent of methyl p-hydroxybenzoate.

15. A facial or bath tissue comprising a polysiloxane and at least  $4.4 \times 10^{-6}$  weight percent methyl p-hydroxybenzoate.

PRESERVED POLYSILOXANE EMULSIONS FOR TREATING TISSUESBackground of the Invention

5           In the manufacture of polysiloxane-treated tissues, the polysiloxane material to be applied to the tissues can be provided as an aqueous emulsion. For purposes of product safety, it is necessary that the emulsion contain a preservative which is effective for inactivating any microorganisms which may be introduced into the  
10           emulsion prior to its use during manufacturing of the treated tissues. Preservative efficacy tests were conducted to determine if a particular preservative was performing adequately. It has been discovered that for certain polysiloxane materials which are particularly useful for treating tissues, the preservatives  
15           ordinarily used for such emulsions are insufficient. More specifically, the polysiloxane emulsions will have a very limited window of utility from the time of synthesis to the time of application to the tissue because of the growth of noxious microorganisms in the emulsions. Although preservatives are added to  
20           the emulsion by the manufacturer, generally those have been found to be of limited value in preventing the growth and proliferation of microorganisms. Because tissue products may be used to directly contact skin around body orifices where the potential for transfer of materials from the tissue to the consumer may constitute a concern,  
25           it is generally good practice to reduce contamination of the tissue in every possible way.

          In addition, of course, preventing the growth and proliferation of microorganisms in the polysiloxane emulsion will also increase the useful shelf life of the product and prevent off-color, off-odor or destruction of the emulsion. Many preservatives  
30           have been tried, but many of these did not provide adequate preservation. Others were ruled out for reasons related to manufacturing or user safety considerations.

### Summary of the Invention

It has now been discovered that aqueous polysiloxane emulsions useful for treating tissues can be preserved effectively if they are at a substantially neutral pH and contain an effective amount of methyl p-hydroxybenzoate, preferably in combination with 2-phenoxyethanol and/or ethylenediaminetetraacetic acid, and more preferably in combination with 2-phenoxyethanol and other p-hydroxybenzoic acid esters. The effective amounts of the preservatives of this invention are those which provide preservative efficacy, either alone or in combination with other preservatives. Efficacy is established when a formulation meets or passes the requirements of the "Standard Test Method for Preservatives in Water-Containing Cosmetics" described in the American Society for Testing and Materials (ASTM) manual (E640-78). It will be appreciated that with respect to the effective amounts of the various species of preservatives within the scope of this invention, the upper limits on the amounts are essentially open-ended because it is generally always possible to add more of the preservative unless solubility, product safety, cost, emulsion stability, etc. become limiting factors on the upper end of the range.

Hence, one aspect of the invention resides in an aqueous polysiloxane emulsion having a pH of from 6.5 to 8, at least 0.1 weight percent ethylenediaminetetraacetic acid, and 0.1 to 1 weight percent of methyl p-hydroxybenzoate. The optimal amount of the methyl p-hydroxybenzoate will depend on the solids content of the silicone emulsion and the other preservative components which are present in the emulsion. As an example of the variability or the effective amount, it has been discovered that a substantially neutralized aqueous polysiloxane emulsion containing about 40 weight percent polysiloxane and 0.5 weight percent methyl p-hydroxybenzoate and 0.5 weight percent ethylenediaminetetraacetic acid (EDTA) is adequately preserved as determined by the efficacy test referred to above. The amount of methyl p-hydroxybenzoate incorporated into this emulsion was unexpectedly high (the water solubility of methyl p-hydroxybenzoate is only about 0.25 weight percent) apparently due to the presence of the polysiloxane. By way of comparison, a much



smaller amount of methyl p-hydroxybenzoate was necessary to effectively preserve the same polysiloxane emulsion when combined with other preservatives. In particular, the emulsion contained about 0.75 weight percent of a preservative mixture containing, on a weight percent basis, of about 70 percent 2-phenoxyethanol, about 15 percent methyl p-hydroxybenzoate, about 6 percent ethyl p-hydroxybenzoate, about 3 percent propyl p-hydroxybenzoate, and about 3 percent butyl p-hydroxybenzoate. This preferred preservative is commercially available from NIPA Laboratories, Inc., Wilmington, Delaware under the tradename PHENONIP.

For aqueous polysiloxane emulsions of this invention containing 2-phenoxyethanol, the effective amount of 2-phenoxyethanol is at least about 0.1 weight percent, preferably from about 0.3 to about 1 weight percent or greater, more preferably from about 0.4 to about 0.7 weight percent, and most preferably about 0.5 weight percent.

For aqueous polysiloxane emulsions containing EDTA, the effective amount of EDTA can be at least about 0.1 weight percent, preferably from about 0.1 to about 1 weight percent or greater.

For aqueous polysiloxane emulsions containing other esters of p-hydroxybenzoic acid, such as ethyl, propyl, butyl, etc., the aggregate amount of these other esters can be at least about 0.01 weight percent and preferably from about 0.01 to about 1 weight percent.

In another aspect, the invention resides in a method for preserving an aqueous emulsion of a polysiloxane polymer or polymer blend comprising: (a) substantially neutralizing the emulsion to a pH of from ~~about~~ 6.5 to ~~about~~ 8, preferably about 7; (b) adding an effective amount of methyl p-hydroxybenzoate, preferably from ~~about~~ 0.1 to ~~about~~ 1 weight percent methyl p-hydroxybenzoate, to the emulsion; and (c) thoroughly mixing the emulsion. Other variations of the method of this invention include adding any of the preservative materials referred to above or any combinations thereof.

In another aspect, the invention resides in a tissue which has been surface-treated with a substantially neutral polysiloxane emulsion containing methyl p-hydroxybenzoate, either alone or in



combination with any of the preservative materials described above.

The dry weight percent add-on amounts of the preservative materials will depend upon the add-on amount of the polysiloxane emulsion and the amount of the preservatives within the emulsion. In general, the

5 add-on amounts will be very small. For methyl p-hydroxybenzoate, the tissue add-on amount can be about  $4.4 \times 10^{-6}$  weight percent or greater, preferably from about  $4.4 \times 10^{-6}$  to about 3 weight percent.

For EDTA, the tissue add-on can be about  $4.4 \times 10^{-6}$  weight percent or greater, preferably from about  $4.4 \times 10^{-6}$  to about 3 weight percent.

10 For 2-phenoxyethanol, the tissue add-on amount can be about  $1.3 \times 10^{-5}$  weight percent or greater, preferably from about  $1.3 \times 10^{-5}$  to about 3 weight percent. For the other esters of p-hydroxybenzoic

acid such as ethyl, propyl and butyl, the aggregate tissue add-on for these species can be about  $4.4 \times 10^{-7}$  weight percent or greater and

15 preferably from about  $4.4 \times 10^{-7}$  to about 3 weight percent.

The aqueous polysiloxane emulsion for treating tissues can contain from about 5 to about 90 weight percent polysiloxane solids, preferably from about 15 to about 65 weight percent. Emulsion tissue add-on amounts can range from about 0.001 to about 300 weight

20 percent, depending upon the polysiloxane content and the desired properties imparted to the tissue. For a 40 weight percent

polysiloxane emulsion, the tissue add-on amount of the emulsion can be from about 0.003 to about 40 weight percent, preferably from about 1.25 to about 12.5 weight percent. Polysiloxanes which are

25 particularly useful for treating tissues in an aqueous emulsion form include those known for their softening effects on cellulosic textile materials, which particularly include silicone fluids which have been modified with various functional groups. Examples of such

30 polysiloxanes include alkyl-, aralkyl-, aryl-, polyalkyleneoxide-, silanic hydrogen-, silanol-, epoxy-, amino-, and mercapto-modified polysiloxanes, as well as blends and copolymers of these

polysiloxanes. Non-reactive polydimethylsiloxanes can also be used, however.

35 Neutralization of the aqueous emulsion, if initially alkaline, can be achieved with any suitable acid. Phosphoric acid is preferred. If the emulsion is initially acidic, sodium hydroxide can

be used to bring the pH up to the desirable level. It has been found that a substantially neutral pH (from about 6.5 to about 8.0) is necessary for the preservative to be effective for such polysiloxane emulsions. A neutral pH is also preferred for reasons related to operator safety in a mill environment in that neutral pH emulsions are less likely to cause skin or eye irritation if contact is made. Preparation of the preserved emulsions of this invention require that the emulsion be thoroughly mixed and homogeneous after the preservative materials are added in order to avoid phase separation and inadequate preservative efficacy.

The following preservatives were tested in accordance with the foregoing ASTM preservative efficacy test in an aqueous polysiloxane (about 40 weight percent) emulsion having a pH of about 10, and failed: (1) SUTTOCID A (1.0%) and methyl p-hydroxybenzoate (0.5%). SUTTOCID A is sodium hydroxymethylglycinate and is commercially available from Sutton Laboratories, Inc., Chatham, N.J.; (2) SUTTOCID A (1.0%) and ethylenediaminetetraacetic acid (EDTA) (0.5%); (3) SUTTOCID A (1.0%) and NUOSEPT 95 (0.3%). NUOSEPT 95 is a mixture of bicyclic oxazolidines, commercially available from Huls America, Inc., Piscataway, N.J.; (4) NUOSEPT 95 (0.3%); and (5) SUTTOCID A (1.0%).

The following preservatives were tested in accordance with the foregoing ASTM preservative efficacy test in an aqueous polysiloxane emulsion which had been neutralized from a pH of about 10 to a pH of about 6-7, and failed: (1) OXABAN A (0.2%) and METHYLPARASEPT (0.1%) and PROPYPARASEPT (0.1%). OXABAN A is dimethyloxazolidine available commercially from Angus Chemical Co., Northbrook, IL. METHYLPARASEPT is methyl p-hydroxybenzoate available commercially from Tennaco Chemical Corp., Piscataway, N.J. PROPYPARASEPT is propyl p-hydroxybenzoate available commercially from Tennaco Chemical Corp., Piscataway, N.J.; (2) OXABAN A (0.1%) and MYACIDE SP (0.1%). MYACIDE SP is dichlorobenzyl alcohol and is commercially available from Boots MicroCheck, Nottingham, U.K.; (3) GERMABEN II E (0.1%). GERMABEN II E is a mixture of 0.1% methyl p-hydroxybenzoate, 0.1% propyl p-hydroxybenzoate, and 0.2% GERMALL II. GERMALL II is diazolidinyl urea available commercially from Sutton Laboratories,



Inc., Chatham, N.J. GERMABEN II E is also available commercially from Sutton Laboratories, Inc.

The following preservatives were considered but rejected for reasons related to product safety: formaldehyde, formaldehyde donors,  
5 QUATERNIUM-15, chloro-methyl-isothiazolinone, methyl-isothiazolinone, and sodium o-phenylphenate.

Hence, because of the rigorous standards which must be met to provide an adequately preserved polysiloxane emulsion for use in treating facial tissues, for example, it was not obvious to identify  
10 a preservative which would satisfy such requirements. As mentioned above, the large majority of the preservatives tested failed to adequately preserve the polysiloxane emulsion.

It will be appreciated that the foregoing examples, given for purposes of illustration, are not to be construed as limiting the  
15 scope of this invention which is defined by the following claims and includes all equivalents thereto.

**The claims defining the invention are as follows:**

1. An aqueous polysiloxane emulsion having a pH of from 6.5 to 8, at least 0.1 weight percent ethylenediaminetetraacetic acid, and 0.1 to 1 weight percent of methyl p-hydroxybenzoate.
- 5 2. The emulsion of claim 1 wherein the amount of ethylenediaminetetraacetic acid is from 0.1 to 1 weight percent.
3. The emulsion of claim 1 wherein the amount of ethylenediaminetetraacetic acid is about 0.5 weight percent.
4. The emulsion of claim 1 further comprising at least 0.1 weight percent  
10 2-phenoxyethanol.
5. The emulsion of claim 4 comprising from 0.1 to 1 weight percent 2-phenoxyethanol.
6. The emulsion of claim 1 further comprising at least 0.01 weight percent of one or more p-hydroxybenzoic acid esters selected from the group consisting of ethyl  
15 p-hydroxybenzoate, propyl p-hydroxybenzoate, and butyl p-hydroxybenzoate.
7. An aqueous polysiloxane emulsion having a pH of from 6.5 to 8 comprising about 0.5 weight percent methyl p-hydroxybenzoate and about 0.5 weight percent ethylenediaminetetraacetic acid.
8. An aqueous polysiloxane emulsion having a pH of from 6.5 to 7.5 comprising  
20 about 0.75 weight percent of a preservative containing about 70 weight percent 2-phenoxyethanol, about 15 weight percent methyl p-hydroxybenzoate, about 6 weight percent ethyl p-hydroxybenzoate, about 3 weight percent propyl p-hydroxybenzoate, and about 3 weight percent butyl p-hydroxybenzoate.
9. A method for preserving an aqueous emulsion of a polysiloxane polymer or  
25 polymer blend comprising:
  - (a) neutralizing the emulsion to a pH of from 6.5 to 8;
  - (b) adding at least 0.1 weight percent methyl p-hydroxybenzoate to the emulsion; and
  - (c) thoroughly mixing the emulsion.
- 30 10. The method of claim 9 wherein the amount of methyl p-hydroxybenzoate is from 0.1 to 1 weight percent.
11. The method of claim 9 further comprising adding to the emulsion at least 0.1 weight percent ethylenediaminetetraacetic acid.
12. The method of claim 11 wherein the amount of ethylenediaminetetraacetic acid  
35 is from 0.1 to 1 weight percent.
13. The method of claim 9 further comprising adding to the emulsion at least 0.01 weight percent of one or more p-hydroxybenzoic acid esters selected from the group consisting of ethyl p-hydroxybenzoate, propyl p-hydroxybenzoate, and butyl p-hydroxybenzoate.



14. The method of claim 13 wherein the aggregate amount of the p-hydroxybenzoic acid esters is from 0.01 to 1 weight percent.

15. A facial or bath tissue comprising a polysiloxane and at least  $4.4 \times 10^{-6}$  weight percent methyl p-hydroxybenzoate.

5 16. The tissue of claim 15 wherein the amount of methyl p-hydroxybenzoate is from  $4.4 \times 10^{-6}$  to 3 weight percent.

17. The tissue of claim 15 further comprising at least  $4.4 \times 10^{-6}$  weight percent ethylenediaminetetraacetic acid.

18. The tissue of claim 17 wherein the amount of ethylenediaminetetraacetic acid  
10 is from  $4.4 \times 10^{-6}$  to 3 weight percent.

19. The tissue of claim 15 further comprising at least  $1.3 \times 10^{-5}$  weight percent 2-phenoxyethanol.

20. The tissue of claim 19 wherein the amount of 2-phenoxyethanol is from  $1.3 \times 10^{-5}$  to 3 weight percent.

15 21. The tissue of claim 15 or 19 further comprising at least  $4.4 \times 10^{-7}$  weight percent of one or more esters of p-hydroxybenzoic acid selected from the group consisting of ethyl p-hydroxybenzoate, propyl p-hydroxybenzoate, and butyl p-hydroxybenzoate.

22. The tissue of claim 21 wherein the amount of the esters is from  $4.4 \times 10^{-7}$  to 3 weight percent.

20 23. An aqueous polysiloxane emulsion substantially as hereinbefore described with reference to any one of the examples.

24. A method for preserving an aqueous emulsion of a polysiloxane polymer or polymer blend substantially as hereinbefore described with reference to any one of the examples.

25 25. A facial or bath tissue substantially as hereinbefore described with reference to any one of the examples.

**Dated 24 August, 1995**  
**Kimberly-Clark Corporation**

**Patent Attorneys for the Applicant/Nominated Person**  
**SPRUSON & FERGUSON**

30



Preserved Polysiloxane Emulsions for Treating Tissues

ABSTRACT OF THE DISCLOSURE

5 Polysiloxane emulsions, useful for treating tissues to improve tactile characteristics, are effectively preserved with at least about 0.1 weight percent of methyl p-hydroxybenzoate. Preferably the preservative further contains one or more p-hydroxybenzoate esters and 2-phenoxyethanol and/or ethylenediaminetetraacetic acid.