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**EMOLLIENT PREPARATIONS CONTAINING  
ALKYLATED POLYMERS OF HETEROCY-  
CLIC N-VINYL MONOMERS**

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**ABSTRACT OF THE DISCLOSURE**

Toiletry and cosmetic compositions are provided which are smooth in texture and which impart a softening and soothing effect to the skin and the appendages of the skin. The said compositions contain as an essential component from 0.1 to about 50% by weight thereof of an alkylated polymer of an N-vinyl heterocyclic monomer wherein on an average at least 25% of the N-vinyl heterocyclic monomer units in said polymer are alkylated with an alkyl group of from 10 to 42 carbon atoms.

This invention relates to emollient preparations containing alkylated polymers of heterocyclic N-vinyl monomers which impart a much smoother texture to the preparation together with a softening and soothing effect when applied to the skin and the appendages of the skin.

It is known that emollients and cosmetics for the skin and hair include all preparations for conditioning or embellishment such as cleansing creams, quick-liquefying creams, emollient creams, cleansing lotions, cream and paste rouges, lipsticks, anti-perspirants, facial masks, massage oils, hair oils and creams, hair removers (epilating wax compositions), eye shadow, sunburn preventives, etc. Many of such preparations, other than normal soap bars, contain petroleum hydrocarbons in one form or another, such as mineral oil, petroleum (solid or liquid), and paraffin wax or a mixture of two or all of such hydrocarbons. Although these preparations are satisfactory for skins and scalps that tend toward oiliness, it is well established that the presence of mineral oils, liquid and solid petrolatums in such preparations is drying to the skin. As a consequence, such preparations require modification with vegetable oils or with cholesterol, lecithin or an absorption base. Paraffin and substances with similar properties are not recommended for use in cosmetic skin preparations because they may clog the pores and cause them to become enlarged or infected. Moreover, many of such preparations are neither sufficiently smooth in texture nor do they impart to the normally dry skin a softening and soothing effect.

The cosmetic industry has and is expending considerable amounts of money in research and development of a product or products which, when incorporated into toiletry preparations, will impart a much smoother texture as well as a softening and soothing effect on the skin and the appendages of the skin. The problems involved are manifold. The cosmetic chemist must consider the nature of the skin, i.e., whether normally dry or oily to which the preparation is to be applied. He must also consider the nature or character of the developed product, its compatibility with other components constituting the preparation and the effect when applied to the skin or the appendages thereof.

It is the principal object of the present invention to provide toiletry preparations, i.e., emollients, cosmetics, and soaps, which are smooth in texture and which impart a softening and soothing effect to the skin and the appendages of the skin.

Another object is to provide cosmetic preparations for the conditioning of nails of the toes and fingers.

A further object is to provide cosmetic preparations for the conditioning and grooming of hair which will leave the hair soft, lustrous, alive-looking and manageable.

Other objects and advantages will become manifest from the following description.

We have discovered that products obtained by the alkylation of polymers of heterocyclic N-vinyl monomers or by the simultaneous polymerization and alkylation of heterocyclic N-vinyl monomers and co-monomers thereof are excellent additives to soaps and cosmetic preparations of the cleansing, conditioning, and embellishing type which will impart a smooth texture as well as a softening and soothing effect to the skin and skin appendages. The additives range from viscous oils to soft and relatively hard waxes. They can be used in place of, and in addition to, petroleum hydrocarbons, i.e., mineral oils, petrolatums and paraffin waxes. They are not only soluble in these petroleum hydrocarbons, but also soluble in other unctuous materials such as fatty acids; stearic, myristic oleic acids, etc.; glyceryl monostearate (Glycoesterin); lanolin (wool fat); beeswax and other animal and vegetable waxes; higher alcohols, such as hexanol, myristyl alcohol, etc.; polyoxyalkylene glycols, e.g., polyoxyethylene glycol, polyoxypropylene glycol; methyl ethyl ketone, Cellosolve (2-ethoxyethanol), butyrolactone, etc., which are employed in toiletry preparations of this type. They are readily emulsified by the usual re-agents employed in toiletry manufacture. By virtue of this solubility, emulsifiability and broad compatibility with other components of the toiletry preparation, they substantially reduce or eliminate the drying tendency of mineral oils and petrolatums present in such preparations. Regardless whether the toiletry preparation contains any one or all of these petroleum hydrocarbons, vegetable oils, lanolin, and/or other unctuous components, or is free from such components, etc., the presence of the additive in such preparation imparts a much smoother texture to it with the attendant softening and soothing effect when applied to the skin and a softening effect when applied to skin appendages.

In some people, overproduction or underproduction of sebum causes excessively oily or excessively dry skin. In very cold weather the sebum congeals on its way to the surface and the skin becomes dry and chapped. In old age, sebum production drops very low and skin fibers lose much of their elasticity. Any toiletry preparation of the cleansing, conditioning or embellishing type containing the additive will keep the skin soft and pliable. Even though the toiletry preparation is removed from the skin or scalp by washing with water and soap, the soft and soothing effect persists. The same effect persists after several washings. The same effect is also noted when the additive is present in hair preparations. The hair remains soft, lustrous and alive-looking. In finger-nail preparations, the additive imparts a softening and soothing effect. In lipsticks, the additive displays dye-binding properties as well as softening and soothing effects. It also retards drying out of the lipstick. In soaps and synthetic soap bars, the presence of the additive imparts a soft and pliable effect on skin and scalp and a soft effect on hair after rinsing with water. The same effect is felt after several rinses with water. Toiletry preparations, especially skin cosmetics, containing the additive and applied to the skin, resist the penetration of oils and of fine dust and other dirt particles which imbed themselves in the skin pores.

The unusual properties of the additive are not clearly understood. The effect upon the skin and scalp, which is quite different from that produced by the petroleum hydrocarbons, lanolin, beeswax, stearic acid, glycerol monostearate, glycerine, the currently used emollients, hair

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oils and creams, etc., may be due to both the hydrophilic character of the

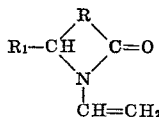


component of the N-heterocyclic ring and the hydrophobic character of the alkyl chain or chains in said ring of the polymer molecule. The hydrophobic character imparts the solubility and compatibility in oils, fats, waxes, and other unctuous materials, as well as smoothness; whereas the hydrophilic character may contribute to the softening and soothing effects.

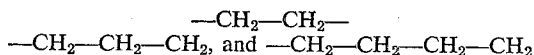
The additives employed in accordance with the present invention are prepared by reacting one mole of a monomer or polymer of a (homopolymer or copolymer) of a heterocyclic N-vinyl monomer with 0.5 to 4, preferably 1 to 3, moles of an  $\alpha$ -olefin of from 10 to 42 carbon atoms in solution of an organic solvent common to the monomer and its polymer (homopolymer or copolymer) in the presence of 0.025 to 0.30 mole of an organic peroxide catalyst per mole of  $\alpha$ -olefin at a temperature ranging from 100° to 200° C. for a period of time ranging from 3 to 60 hours. The percent of  $\alpha$ -olefin reacted is determined by the percent of the  $\alpha$ -olefin consumed and may range from about 50% to 100% of the  $\alpha$ -olefin charged. Alkylated polymers of heterocyclic N-vinyl monomers with emollient properties are obtained in which a minimum of 25% to a maximum of 400% of the monomeric units in the polymer are alkylated. In other words, alkylated homopolymers are obtained containing an average of 0.25 to 4 alkyl groups of 10 carbon atoms per monomer unit. In the case of a copolymer of 60% by weight of heterocyclic N-vinyl monomer and 40% by weight of a non-heterocyclic monomer, alkylated copolymers with emollient properties are obtained in which a minimum of 30% to a maximum of 240% of the heterocyclic N-vinyl units in the copolymer are alkylated, i.e., containing at least 0.25 alkyl groups of 10 carbon atoms per monomeric unit in the copolymer. In alkylating such copolymers to obtain the best emollient properties, it is preferred that 1-3 moles of  $\alpha$ -olefin be reacted with one mole of copolymer to yield an alkylate in which at least 30% of the heterocyclic N-vinyl units in the copolymer are alkylated. The resulting solution of the alkylated polymer is subjected to vacuum distillation to remove the organic solvent. The residue, alkylated polymer, ranges from a viscous oil to a soft and substantially hard wax.

The homopolymers of heterocyclic N-vinyl monomers, which are alkylated with an  $\alpha$ -olefin of from 8 to 42 carbon atoms and employed as additives, include homopolymers of N-vinyl succinimide, N-vinyl diglycolylimide, N-vinyl glutarimide, N-vinyl-3-morpholinone, N-vinyl-5-methyl-3-morpholinone, N-vinyl-5-ethyl-3-morpholinone, and N-vinyl lactams having the following formulae:

(1)



wherein R represents an alkylene bridge, i.e.,

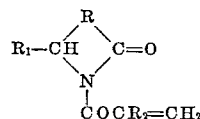


to complete a 5-, 6-, and 7-membered heterocyclic ring system and R<sub>1</sub> represents either hydrogen, methyl or ethyl. Such homopolymers are obtained by polymerizing N-vinyl 5-, 6-, and 7-membered ring compounds such as, for example, N-vinyl-2-pyrrolidone, N-vinyl-5-methyl-2-pyrrolidone, N-vinyl-5-ethyl-2-pyrrolidone, N-vinyl-2-piperidone, N-vinyl-6-methyl-2-piperidone, N-vinyl-6-ethyl-2-piperidone, N-vinyl- $\epsilon$ -caprolactam, N-vinyl-7-methyl- $\epsilon$ -caprolactam and N-vinyl-7-ethyl- $\epsilon$ -caprolactam. Comparable homopolymers are obtainable from the corresponding

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N-vinyl thiolactams and these can be used in the alkylation process.

(2)



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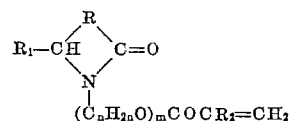
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wherein R<sub>2</sub> represents either hydrogen or methyl group and R and R<sub>1</sub> have the same value as above. Illustrative compounds, obtained by the conventional reaction of a 5-, 6-, or 7-membered lactam with acryloyl or methacryloyl chloride or bromide in the presence of a hydrogen halide acceptor such as pyridine, dimethylaniline, etc., are N-methacryloyl-pyrrolidone, -piperidone and -caprolactam; N-methacryloyl-5-methylpyrrolidone, N-methacryloyl-6-methylpiperidone and N-methacryloyl-7-methyl caprolactam and their corresponding 5-, 6-, and 7-ethyl derivatives; N-acryloyl-pyrrolidone, -piperidone and -caprolactam; N-acryloyl-5-methylpyrrolidone, N-acryloyl-6-methylpiperidone and N-acryloyl-7-methyl caprolactam and their corresponding 5-, 6- and 7-ethyl derivatives; acrylic esters having the structure:

(3)



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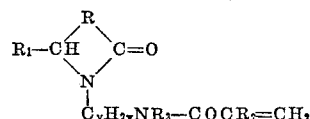
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wherein R, R<sub>1</sub> and R<sub>2</sub> have the same values as above, *m* is an integer of from one to four, and *n* is an integer of from one to four when *m* has a value of one and from two to four when *m* has a value greater than one. Illustrative compounds are N-acryloxy-methyl-pyrrolidone, -piperidone and -caprolactam; N-methacryloxy-ethoxy-ethyl-pyrrolidone, -piperidone and -caprolactam; N-methacryloxy-propyl-pyrrolidone, -piperidone and -caprolactam; N-methacryloxy-ethyl-pyrrolidone, -piperidone, and -caprolactam; N-methacryloxy-methyl-5-methyl-pyrrolidone, -6-methylpiperidone and -7-methyl-caprolactam, including amidoalkyl lactams of the structure:

(4)



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wherein R, R<sub>1</sub> and R<sub>2</sub> have the same value as above, R<sub>3</sub> represents hydrogen, alkyl group of from 1 to 12 carbon atoms or phenyl, and Y represents an integer of from 2 to 3. Illustrative compounds of this type are N-methacrylamidomethyl-, N-methacrylamidoethyl-, N-methacrylamidopropyl and N-(N-phenylacrylamidopropyl)-pyrrolidones, -piperidones and -caprolactams, which are readily prepared by reacting acryloyl or methacryloyl chloride or bromide with an N-(aminoalkyl)-lactam, wherein the alkyl is from 1 to 12 carbon atoms, in the presence of any conventional base to take up the hydrogen halide.

The individual homopolymers of the foregoing heterocyclic N-vinyl monomers may be alkylated as such or in admixture. The proportions constituting the mixture are immaterial since such mixture of homopolymers is readily alkylated and yields a product with emollient properties. However, where a mixture of any one of the foregoing heterocyclic N-vinyl monomers is copolymerized prior to alkylation with an  $\alpha$ -olefin, with a non-heterocyclic monomer containing a polymerizable vinyl group, it is preferable that the comonomer mixture contain at least 60% by weight, i.e., from 60% to 95% by weight of any one of the foregoing heterocyclic N-vinyl monomers with up to 40% by weight, i.e., from 5 to 40% by weight of a non-heterocyclic monomer. The non-heterocyclic monomers containing a polymerizable vinyl group which are copolymerized with any one of the foregoing heterocyclic N-vinyl monomers, prior to alkylation, including

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vinyl ester monomers such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, vinyl lactate, vinyl caproate, vinyl caprylate, vinyl oleate, and vinyl stearate; vinyl chloride; vinylidene chloride; acrylonitrile; styrene; acrylic acid; acrylic ester monomers of the formula



wherein R<sup>1</sup> represents either a straight or branched alkyl of from 1 to 18 carbon atoms or an alkoxyalkyl in which the total number of carbon atoms in the alkyl groups range from 3 to 6. As examples of such acrylate esters the following are illustrative: methyl, ethyl, propyl, isopropyl, butyl, isobutyl, s-butyl, 2-methyl-1-butyl, 3-methyl-1-butyl, 2-ethyl-1-butyl, amyl, 3-pentyl, 2-methyl-1-pentyl, 4-methyl-2-pentyl, hexyl, 2-ethylhexyl, heptyl, 2-heptyl, octyl, 2-octyl, nonyl, 5-ethyl-2-nonyl, decyl, 2-methyl-7-ethyl-4-undecyl, dodecyl, tetradecyl, hexadecyl, octadecyl, 2-methoxyethyl, 2-ethoxyethyl and 2-butoxyethyl acrylate; methacrylate monomers such as methacrylic acid, methyl methacrylate, cyclohexyl methacrylate, isobutyl methacrylate, isoamyl methacrylate,  $\beta$ -methoxyethyl methacrylate and  $\alpha$ -(o-chlorophenyl) ethyl methacrylate,  $\beta$ -phenoxyethyl methacrylate,  $\alpha$ -phenylethyl methacrylate, phenyl methacrylate, o-cresyl methacrylate, p-cyclohexylphenyl methacrylate, 2-nitro-2-methyl propyl methacrylate, diethylaminoethyl methacrylate, ethylidene acetate methacrylate and glycidyl methacrylate, including esters of halo acrylic acids, such as methyl- $\alpha$ -chloroacrylate, ethyl- $\alpha$ -chloroacrylate, phenyl- $\alpha$ -chloroacrylate,  $\alpha$ -ethylacrylic acid; methacrylonitrile; acrylamide; methacrylamide, as well as N-alkyl and N-aryl substituted acrylamides such as N-methyl acrylamide, N-ethyl acrylamide, N-propyl acrylamide, N-n-butyl acrylamide, N-n-dodecyl acrylamide, N-n-octadecyl acrylamide, N,N-dimethyl acrylamide, N,N-diethyl acrylamide, N,N-di-n-butyl acrylamide, N,N-diisobutyl acrylamide, N-cyclohexyl acrylamide, N,N-dicyclohexyl acrylamide, N-phenyl acrylamide, N-p-nitrophenyl acrylamide, N- $\alpha$ -naphthyl acrylamide, N- $\beta$ -naphthyl acrylamide, N-methyl-N-phenyl acrylamide, N,N-diphenyl acrylamide, N-benzyl acrylamide, N,N-dibenzyl acrylamide; and grafted monomers on the polyvinyl lactam of the type disclosed in United States Patents 3,029,219; 3,035,009; 3,036,033, and the like. Both the homopolymers and copolymers should have a K value of 10 to 140 for the alkylation reaction, preferably of 20 to 100.

It is to be noted that the nature or character of the non-heterocyclic polymerizable monomers is immaterial so long as such monomers are capable of copolymerization in the aforesaid proportions with the heterocyclic N-vinyl monomers and yield copolymers which can be alkylated.

In the alkylation of the polymers of heterocyclic N-vinyl monomers, i.e., homopolymers and copolymers, any  $\alpha$ -olefin having a molecular weight from about 140 to about 588 may be employed in the alkylation reaction. In other words, alpha-olefins (straight chain or branched), ranging from 1-dodecene, 1-tetradecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-docosene, 1-tetracosene, 1-pentacosene to trimerized  $\alpha$ -tetradecene may be used.

While linear  $\alpha$ -olefins are preferred because of their commercial availability, numerous isomers of  $\alpha$ -olefins ranging from 1-pentene to 1-pentacosene as well as polybutenes may also be employed in the alkylation reaction. The only precaution required in such case is that the isomer contain an ethylenic unsaturation in the  $\alpha$ -position thereof.

Instead of employing any one of the foregoing individual  $\alpha$ -olefins; a mixture of commercially available linear  $\alpha$ -olefins produced by cracking petroleum wax or by polymerizing lower olefins may also be used as the alkylating agent. The commercial product composition contains a mixture of linear olefins ranging from 11 to 15 carbon atoms, and as high as 15 to 22 carbon atoms.

In lieu of the individual  $\alpha$ -olefins of from 10 to 42 carbon

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atoms or mixtures thereof, alkylated polymers of heterocyclic N-vinyl monomers suitable for the purpose of the present invention are also obtained by alkylating the polymer (homo- and co-polymer) with at least 5 moles to as high as 16 moles of ethylene for each mole of polymer to yield an alkylate wherein the ethylene propagates itself to a minimum average chain length of 10 carbon atoms. A minimum average chain length of 10 carbons is also obtained by alkylation with 1-propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene or 1-nonene. In determining for each mole of polymer the required number of moles of such  $\alpha$ -olefin, i.e., from 2 to 9 carbon atoms to obtain the minimum average chain length of 10 carbon atoms, the following formula may be used:

$$\text{MC}=10$$

wherein M represents the number of moles of the  $\alpha$ -olefin and C represents the number of carbon atoms in the  $\alpha$ -olefin.

Instead of employing ethylene as the alkylating agent, chlorinated and/or fluorinated  $\alpha$ -olefins such as, for example, dichlorovinylidene fluoride, chlorovinylidene fluoride, chlorotrifluoroethylene, tetrafluoroethylene, vinylidene fluoride and the like may be used.

In the alkylation of polymeric heterocyclic N-vinyl compounds with an alpha-olefin or mixtures thereof, an organic solvent is employed which is common to the polymer and alpha-olefin(s). As solvents, various alcohols such as methanol, ethanol, propanol, isopropanol, butanol, sec-butanol, amyl alcohol, hexanol, 2-ethyl-1-hexanol, ethylene glycol, 1,2-butanediol, 4-butanediol, etc. may be employed. Other solvents such as diacetone alcohol, diethylene glycol, ethylene glycol monomethyl ether acetate, methylene chloride and the like may also be employed. It is to be noted that the nature or character of the organic solvent is immaterial so long as it is a liquid, forms a solution with the polymer and alkylating  $\alpha$ -olefin(s), and is not susceptible to alkylation.

The amount of organic solvent employed is not critical. Any amount which will yield a solution of the polymeric material and  $\alpha$ -olefin(s) will suffice. However, for purposes of expediency, for every part by weight of solid homopolymer or copolymer of N-vinyl lactam, from 2 to 10 parts of organic solvent, either by volume or by weight, are sufficient to yield a workable solution.

As peroxide catalyst (initiator) for the alkylation reaction, any one of the known tertiary-alkyl organic peroxides such as, for example, t-butyl hydro-peroxide, di-t-butyl peroxide, t-butyl perbenzoate, di-ti-butyl peroxide, t-butyl perbenzoate, di-ti-butyl perphthalate, t-butyl-pentamethyl-ethyl peroxide, t-butyl-triphenylmethyl peroxide, di-t-amyl peroxide, bis-(triethylmethyl) peroxide, bis-(triphenylmethyl) peroxide, 2,5-dimethylhexyl-2,5-dihydro-peroxide, 2,5-dimethyl-2,5-di(t-butyl peroxy) hexane, 2,5-dimethylhexyl-2,5-di(peroxy benzoate), and the like may be used.

The alkylation procedure for both the homopolymers and copolymers of the foregoing heterocyclic N-vinyl monomers is more fully described in the co-pending applications of Ashot Merijan, Frederick Grosser and Eugene Hort, Ser. No. 340,786, filed on Jan. 28, 1964, entitled "Process of Alkylating Polymer N-Vinyl Lactams," now abandoned, the complete disclosure and teachings of which are incorporated herein by reference thereto. Alkylated homopolymers and copolymers with emollient properties are also obtained by the procedure described in the co-pending application of Ashot Merijan and Frederick Grosser, Ser. No. 358,406, filed on Apr. 8, 1964, and entitled, "Simultaneous Polymerization and Alkylation of Heterocyclic N-Vinyl Monomers," now abandoned, the complete disclosure and teachings of which are incorporated herein by reference thereto.

Where it is desired that the alkylated polymer be in solution of a mineral oil of the type employed in toiletries, the alkylation of the polymers or the simultaneous polymerization and alkylation reaction of the monomer(s) is

preferably conducted in the presence of hexanol. As the latter is being removed during vacuum distillation, it is replaced with a refined mineral oil and the resulting solution of the alkylated polymer employed as the additive. Any refined mineral oil used by the pharmaceutical and cosmetic trade is ideally suited as a replacement during the removal of the hexanol by vacuum distillation.

The following examples will show how some of the alkylated polymeric N-vinyl lactams are prepared.

## EXAMPLE I

Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet, and reflux condenser, the following ingredients were charged and the system then purged with nitrogen:

|   | Grams |
|---|-------|
| Polyvinyl-2-pyrrolidone (K-30) (1.0 mole) ----- | 111   |
| $\alpha$ -Eicosene ----- (1.0 mole) --          | 280   |
| Methyl isobutyl carbinol -----                  | 200   |
| Di-t-butyl peroxide ----- (0.1 mole) --         | 14.6  |

The contents were maintained at 130–135° C. for 16 hours and then a second addition of 7.3 grams (0.05 mole) peroxide was made and reaction continued for eight more hours. (Total peroxide=21.9 grams, 0.15 mole.) The solution was cooled and analyzed. The analytical data showed only 5.48% of unreacted  $\alpha$ -eicosene. The contents were subjected to vacuum distillation and the methyl isobutyl carbinol removed. A waxy solid weighing about 350 grams was obtained.

## EXAMPLE II

Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, the following materials were charged:

|  | Grams |
|--|-------|
| Polyvinyl-2-piperidone (K-30) ---- (1.0 mole) -- | 125   |
| $\alpha$ -Octadecene ----- do -----              | 252   |
| Normal butanol -----                             | 200   |
| Di-to-butyl peroxide ----- (0.1 mole) --         | 14.6  |

The flask was purged thoroughly with nitrogen and heated. The contents were maintained at reflux (120° C. pot) for 30 hours and then cooled and analyzed. The analyses showed the presence of only 3.05% of  $\alpha$ -octadecene in the solution, corresponding to 18 grams unreacted olefin.

When all the n-butanol was stripped in vacuum, a very clear, oily, somewhat hard gel, weighing about 353 grams, was obtained.

## EXAMPLE III

Into a one-liter, four-necked reaction flask, equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, the following materials were charged:

|  | Grams |
|--|-------|
| Polyvinyl- $\epsilon$ -caprolactam (K-30) ---- (1.0 mole) -- | 139   |
| $\alpha$ -Octene ----- do -----                              | 112   |
| Methyl isobutylcarbinol -----                                | 200   |
| Di-t-butyl peroxide ----- (0.09 mole) --                     | 13.1  |

The flask was then purged thoroughly with nitrogen, heated and maintained at 125–135° C. for 24 hours. The contents when analyzed showed the presence of only 4.54% of  $\alpha$ -octene, corresponding to about 21 grams of the unreacted olefin. The solvent was stripped in vacuum and about 210 grams of a clear, oily gel was obtained.

## EXAMPLE IV

Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, the following materials were charged:

|  | Grams |
|--|-------|
| Polyvinyl-2-pyrrolidone (K-30) ---- (0.5 mole) --  | 55.5  |
| $C_{42}$ $\alpha$ -olefin obtained by the trimerization of $\alpha$ -tetradecene ----- (0.5 mole) -- | 294   |
| Methyl isobutylcarbinol -----  | 120   |
| Di-t-butyl peroxide ----- (0.1 mole) --  | 15    |

The flask was purged thoroughly with nitrogen and heated. The contents were maintained at reflux for 24 hours and then cooled and analyzed. The analysis showed the presence of 7.75% of the  $C_{42}$   $\alpha$ -olefin in the solution corresponding to 37.5 grams of unreacted olefin.

When all the solvent was stripped in vacuum, about 350 grams of a white wax were obtained.

## EXAMPLE V

Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, after a thorough nitrogen purge, the following ingredients were charged and heated:

|   | Grams |
|---|-------|
| Polyvinyl-5-methyl-2-pyrrolidone (K-45) ----- (1.0 mole) -- | 125   |
| Hexanol (mixture of isomeric hexanols) -----                | 200   |
| $\alpha$ -Octadecene ----- (1.0 mole) --                    | 252   |
| Di-t-butyl peroxide ----- (0.1 mole) --                     | 15    |

The solution was maintained at 120–140° C. for 30 hours and then cooled and analyzed. It was found to contain only 4.56%  $\alpha$ -octadecene, corresponding to 27 grams, or a 89.4% consumption of the  $\alpha$ -olefin charged. When the solvent was removed in vacuum, about 348 grams of a waxy material were obtained.

## EXAMPLE VI

A 70/30 (by weight) copolymer of N-vinyl piperidone and vinyl acetate weighing 100 grams was dissolved in 200 grams of hexanol followed by the addition of 280 grams (1.0 mole) of  $\alpha$ -eicosene and 14.6 grams (0.1 mole) of di-t-butyl peroxide. The mixture was heated to 120–130° C. and maintained for 24 hours. The product, after cooling, was analyzed and found to contain 3.73% of  $\alpha$ -eicosene corresponding to 92% alkylation based on the olefin charged. The product is a relatively hard waxy substance.

## EXAMPLE VII

An 80/20 (by weight) copolymer of N-vinyl- $\epsilon$ -caprolactam and ethyl acrylate weighing 100 grams was dissolved in 200 grams of normal amyl alcohol and after the addition of 252 grams (1.5 mole) of  $\alpha$ -dodecene and 22 grams (0.15 mole) of di-t-butyl peroxide, the solution was heated and maintained at 120°–140° C. for 10 hours. The reaction mixture was then cooled and analyzed. It was found to contain 4.2% of unreacted  $\alpha$ -dodecene, corresponding to 90.5% alkylation based on the dodecene used. The product is a soft waxy substance.

## EXAMPLE VIII

Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, the following materials were charged:

|  | Grams  |
|--|--------|
| Polyvinyl-2-pyrrolidone (K-60) --- (1.0 mole) -- | 111    |
| $\alpha$ -Octene ----- (2.0 mole) --             | 224.42 |
| Normal butanol -----                             | 200    |
| Di-t-butyl peroxide ----- (0.2 mole) --          | 29.2   |

The flask was purged thoroughly with nitrogen and heated. The contents were maintained at reflux for 30 hours and then cooled and analyzed. The analysis showed the presence of only 4.97% of  $\alpha$ -octene in the solution corresponding to 28 grams of unreacted olefin.

When all the solvent was stripped in vacuum and substituted with 450 grams of refined mineral oil (pharmaceutical grade), a very clear, oily solution, weighing 751 grams was obtained.

## EXAMPLE IX

Example I was repeated with the exception 1 mole of  $\alpha$ -eicosene was replaced by 1 mole of a commercial mixture of  $\alpha$ -olefins in the  $C_{15}$ – $C_{20}$  carbon range. The product is a waxy substance.

## EXAMPLE X

Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, the following ingredients were charged:

|  | Grams |
|--|-------|
| N-vinyl-2-pyrrolidone ----- (0.5 mole) --  | 55.5  |
| N-vinyl-3-morpholinone ----- do -----      | 63.5  |
| Methyl isobutylcarbinol -----              | 200   |
| $\alpha$ -Octadecene ----- (1.25 mole) --  | 315   |
| t-Butyl hydroperoxide ----- (0.12 mole) -- | 11    |

The flask was purged with nitrogen thoroughly and heated. The contents were maintained at 130–140° C. for 12 hours and then 11.0 more grams of peroxide were added and heated continually for another 12 hours. (Total peroxide=22 grams or 0.24 mole.) In analysis of the contents, no trace of N-vinyl-2-pyrrolidone or N-vinyl-3-morpholinone were found but only the presence of 11.6% of  $\alpha$ -octadecene was detected which indicates a residual of 76 grams unreacted olefin. The contents were then transferred into a two-liter flask and the solvent stripped in vacuum and substituted with 434 grams 100 sec. solvent. The final 50% solution was a clear amber liquid weighing 860 grams.

## EXAMPLE XI

Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, the following ingredients were charged:

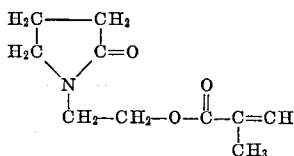
|   | Grams |
|---|-------|
| N-vinyl succinimide ----- (0.5 mole) -- | 62.5  |
| Methyl isobutylcarbinol -----           | 150   |
| $\alpha$ -Eicosene ----- (0.65 mole) -- | 182   |
| Di-t-butyl peroxide ----- (0.1 mole) -- | 15    |

The flask was purged with nitrogen, heated and maintained at a range of 120–140° C. for 30 hours. The contents were then cooled and analyzed and found to contain only a trace of N-vinyl succinimide and 3.66% (equivalent to 15.0 grams unreacted only) of  $\alpha$ -eicosene by weight of the solution. Then 244.5 grams of 100 sec. solvent were added and the solvent stripped in vacuum. The final 50% solution obtained was clear and weighed 485 grams. (Theory=489.0 grams.)

## EXAMPLE XII

Into a one-liter, four-necked flask equipped with stirrer, thermometer, nitrogen inlet and reflux condenser, after a thorough nitrogen purge, the following ingredients were charged and heated:

N-methacryloyloxyethylpyrrolidone=46.0 gr. (0.23 mole)



|  | Grams |
|--|-------|
| N-butanol -----                        | 200   |
| $\alpha$ -Eicosene ----- (0.5 mole) -- | 140   |
| Di-t-butyl peroxide -----              | 10    |

The mixture (clear phase) was maintained at reflux (117–125° C.) for 20 hours and then another 5.0 grams peroxide added (total peroxide=15.0 grams, 0.1 mole) and refluxing continued for 16 more hours. The contents were then cooled and analyzed. The analysis showed the total absence of the monomer and only 3.0% (equivalent to 12.0 grams unreacted) of  $\alpha$ -eicosene. The solvent was then stripped in vacuum and substituted with 186 grams 100 sec. solvent. The final 50% solution in the 100 sec. solvent was clear and weighed 371 grams. (Theory=372 grams.)

The alkylated polymers of heterocyclic N-vinyl monomers prepared as above described, and in accordance with the foregoing illustrative examples, are soluble in all of

the unctuous materials used in toiletry preparations such as vegetable and mineral oils, fatty acids, fatty acid esters, waxes, polyoxyalkylene glycols, higher alcohols of from 6 carbon atoms and up, including compounds having similar boiling points of the type employed in the alkylation reaction. They are also partially soluble in hot lower alcohols such as ethanol and propanol. Solutions of the product of Example I in hot ethanol and in hot propanol are cooled to room temperature, the ethanol contains about 0.1% of alkylated polymer, whereas the propanol contains about 0.3% of the alkylated polymer. Their partial solubility in such alcohols provides an excellent means for incorporation into non-unctuous materials. The alkylated polymers are added at any suitable stage of conventional toiletry manufacture. In other words, if the toiletry preparation comprises an unctuous base the alkylated polymer is dissolved in such base by gentle heating and stirring until solution is attained. For example, where such unctuous material is a liquid such as mineral oil, myristyl alcohol, etc., the alkylated polymer is dissolved therein at room temperature with or without gentle heating and stirring. Where such unctuous components are solids such as solid petrolactams, paraffin wax, natural and synthetic waxes, fatty acid, fatty acid esters, lanolin, etc., they are first heated to the liquid state and the alkylated polymer dissolved therein with stirring. The temperature of heating may vary from 50° to 100° C., depending upon the nature or character of the unctuous material. If a water phase is included in such preparation such as triethanolamine, borax, sodium or potassium hydroxide, and any other water soluble components, the oil phase is added slowly to the water phase or vice versa with good agitation.

The amount of alkylated polymer that is employed to effect the desired results (smoother texture with softening and soothing effects) ranges from about 0.1% to about 50% by weight based on the total weight of the completed toiletry preparation. The alkylated polymers are added at any stage of manufacture of cold creams, cleansing creams, emollient creams, finishing creams, skin-softening lotions, hand cleaners, lubricating creams, overnight creams, absorption-base creams, hand creams and lotions, foot creams, baby creams, baby skin oils; special creams, such as astringent creams, bleaching creams, acne creams, protective creams (industrial creams), vanishing creams, foundation creams, brushless shaving creams, shaving preparations, after-shave lotions and sprays, medicated creams, deodorants and anti-perspirants, such as deodorant creams and lotions, roll-on deodorants, sunburn preventives, suntan preparations, paste or lotion rouges, cream rouges, massage oils, facial masks, depilatories, i.e. hair removers (epilating wax compositions) and hair removing creams, paste or lotion face make-up, face powders; eye makeup, i.e., eye shadows and eyebrow creams; fingernail creams and cleaners, hair bleaches and tints, cuticle softeners, hair conditioners, wave sets, hair dressings, hair brilliantines; hair oils, hair sprays, creams and shampoos, nail polish removers, lipsticks, perfume sticks, facial soaps, synthetic soap bars, antiseptic soaps (tincture of green soap), insect repellents, protective hand creams, waterless hand cleaners, dentifrice, pet shampoos, bath talcs, and the like.

The alkylated polymers are effective pigment dispersers and act as color receptors. In hair preparations the presence of the alkylated polymer improves the softness, water repellency and manageability of the hair. In hair conditioners, the alkylated polymers may be added to creams, foams or gels and the resulting preparations pressurized with nitrogen, argon, or the usual liquefied fluorochloro-hydrocarbons.

In each of the following toiletry preparations, the presence of the alkylated polymer rendered the preparation smoother in texture and easier in application to the skin and its appendages (hair and nails). After application to the skin or scalp, the preparations left the skin soft and

pliable with a soothing effect which remained after the preparation was removed by washing with soap and water. After application to the hair, the preparation deposited a film which rendered the hair soft, smooth, lustrous and alive-looking. The soft and smooth effects remained after washing with soap and water and enhanced the manageability of the hair. After application of the nail preparations, the nails were smooth and the adjacent skin rendered soft and pliable with a soothing effect.

**EXAMPLE XIII**

## Cold cream

52 grams of liquid petroleum, 14 grams of beeswax and 5 grams of the alkylated polymer of Example I were heated on a steam bath to 87° C. in a 250 ml. beaker and stirred with a small propeller-type stainless steel stirrer for about five minutes until the beeswax had completely dissolved.

1 gram of borax (sodium tetraborate) was dissolved in 33 ml. of water by heating to the boil in a 100 ml. beaker. The borax solution was poured in a small steady stream into the white mineral oil-beeswax-additive-solution which was being rapidly stirred. The hot solution was cooled to 49° C. and poured into three 1-ounce bottles and then allowed to cool to room temperature.

**EXAMPLE XIV**

## Brushless shaving cream

10 grams of white mineral oil, 10 grams of glyceryl monostearate and 3.5 grams of the alkylated polymer of Example I were creamed on a steam bath with stirring to 66° C. for 10 minutes or until a complete solution had resulted. With very rapid stirring, by a stainless steel propeller type stirrer, 50 ml. of boiling distilled water was slowly added in a small stream. Rapid stirring was continued while allowing the cream to cool to room temperature. The brushless shaving cream was transferred to a suitable glass jar.

**EXAMPLE XV**

## Hand lotion (liquid)

5 grams of boric acid was dissolved in 30 grams glycerine by heating the mixture in a 100 ml. beaker to 105° C. with an electromagnetic-type electrically heated stirrer. 30 grams of lanolin and 10.5 grams of the alkylated polymer of Example I were dissolved in 40 grams of white mineral oil in a 250 ml. beaker by heating to 60° C. on a steam bath while stirring with a small stainless steel stirrer. After 10 minutes stirring at 60° C., and after the lanolin and additive had completely dissolved, the glycerine solution of boric acid was slowly added in a thin stream to the solution of lanolin, additive and mineral with rapid agitation.

**EXAMPLE XVI**

## Vanishing cream

36 grams of stearic acid were melted by heating on a steam bath at 90° C. with continual agitation by a stainless steel stirrer. 6 grams of the alkylated polymer of Example I were dissolved in the molten stearic acid. 13 grams of glycerine and 0.5 gram of potassium carbonate were dissolved in 50 mls. of boiling water. The boiling aqueous solution was added gradually to the molten stearic acid and additive which was being stirred at a very fast speed. Fast agitation was continued while the mixture was allowed to cool to room temperature.

**EXAMPLE XVII**

## Cleansing cream

10 grams of petrolatum, 27.5 grams of white mineral oil, 12.5 grams of paraffin wax and 5 grams of the alkylated polymer of Example I were melted together in a 100 ml. beaker while stirring and heating on a steam bath to

72° C. The melted solution was poured into a glass jar and allowed to cool undisturbed overnight.

**EXAMPLE XVIII**

## Hand lotion (salve)

2 grams of boric acid were dissolved in 12 grams of glycerine by heating to 105° C. with stirring in a 30 ml. beaker. 16 grams of petrolatum, 12 grams of lanolin and 42 grams of the alkylated polymer of Example I were melted and dissolved in each other by heating to 70° C. while stirring in a 100 ml. beaker. The boric acid-glycerine solution was added slowly to the petrolatum-lanolin-additive-solution with continual stirring with a stainless steel agitator. The hot (80° C.) molten salve was poured into a jar and allowed to cool undisturbed to room temperature.

**EXAMPLE XIX**

## Emollient cream

This cream was prepared from the following ingredients in percent by weight:

|                                       | Grams |
|---------------------------------------|-------|
| Beeswax -----                         | 8     |
| Cetyl alcohol -----                   | 2     |
| Cocoa butter -----                    | 2     |
| Lanolin (anhydrous) -----             | 10    |
| Olive oil -----                       | 50    |
| Lecithin -----                        | 1     |
| Alkylated polymer of Example II ----- | 7     |

were dissolved in admixture by heating to 87° C. The resulting solution was allowed to reach room temperature to which was added 1 gram of rose perfume. Sufficient distilled water was added with agitation to make 100 parts by weight of finished emollient cream.

**EXAMPLE XX**

## Quick-liquefying cream

|  | Percent by weight |
|--|-------------------|
| Mineral oil -----                      | 40                |
| Paraffin wax -----                     | 18                |
| Beeswax -----                          | 9                 |
| Petrolatum -----                       | 23                |
| Alkylated polymer of Example III ----- | 10                |

The foregoing components were heated to 87° C. with stirring. The hot solution was poured into a jar and allowed to cool to room temperature.

**EXAMPLE XXI**

## Paste rouge

|   | Percent by weight |
|---|-------------------|
| Ceresin -----   | 20                |
| Mineral oil -----                                       | 45                |
| Petrolatum -----  | 21                |
| Spermaceti -----  | 3                 |
| Finely divided certified color -----                    | 1                 |
| Oil solution of alkylated polymer of Example VIII ----- | 10                |

The above mixture was heated to 85° C. in a stainless steel beaker until all components were dissolved. The mixture was allowed to cool about the solidification point and the mass run through an ointment mill and poured into a container.

**EXAMPLE XXII**

## Lipstick

|                                       | Percent by weight |
|---------------------------------------|-------------------|
| Beeswax -----                         | 10                |
| Carnauba wax -----                    | 3                 |
| Ceresin -----                         | 10                |
| Mineral oil -----                     | 10                |
| Petrolatum -----                      | 49                |
| Alkylated polymer of Example IV ----- | 5                 |
| Lakes (dibromofluorescein) -----      | 13                |



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The oil phase was heated to yield a solution. The color was added and the mixture cooled above the solidification point and poured in lipstick molds.

## EXAMPLE XXIII

## Anti-perspirant stick

|                                      | Percent by weight |
|--------------------------------------|-------------------|
| Alum .....                           | 5                 |
| Beeswax .....                        | 20                |
| Lanolin .....                        | 6                 |
| Hydroxyquinoline sulfate .....       | 2                 |
| Petrolatum .....                     | 30                |
| Mineral oil .....                    | 10                |
| Titanium dioxide .....               | 2                 |
| Talc .....                           | 15                |
| Zinc phenol sulfonate .....          | 5                 |
| Alkylated product of Example V ..... | 5                 |

The oil phase was heated to the liquid state and the mixture of alum, hydroxyquinoline sulfate, titanium dioxide, talc and zinc phenol sulfonate added with stirring. The resulting mixture was allowed to cool above the solidification point and poured into stick molds and the sticks mounted in a suitable holder.

## EXAMPLE XXIV

## Synthetic soap bar

30% by weight of stearic acid and 10% by weight of the alkylated polymer of Example I were melted and emulsified with 8% by weight of water. To the emulsion were added, with agitation, 30% by weight of myristic sodium isethionate, 5% by weight of ethoxylated nonyl phenol containing 80% by weight of ethylene oxide and 20% by weight of sodium tallowate. The resulting mixture was cooled and subjected to soap bar formation by the conventional injection molding.

## EXAMPLE XXV

## Total sunscreen lotion

|  | Percent by weight |
|--|-------------------|
| Mineral oil .....                                    | 40.0              |
| Beeswax .....  | 6.0               |
| Oil solution of alkylated polymer of Example X ..... | 19.5              |
| Water .....  | 33.5              |
| 2,2', 4,4'-tetrahydroxy-benzophenone .....           | 0.5               |
| Sodium hydroxide .....                               | 0.5               |

The oil phase and alkylated polymer were heated to 70° C. and the water phase, including the sunscreen agent and sodium hydroxide to the same temperature. The oil phase was added slowly to the water phase with good agitation. A creamy emulsion resulted.

## EXAMPLE XXVI

## Hair shampoo

|                                       | Percent by weight |
|---------------------------------------|-------------------|
| Stearic acid .....                    | 3.5               |
| Myristic acid .....                   | 2                 |
| Oleic acid .....                      | 2.5               |
| Alkylated polymer of Example IX ..... | 1.8               |
| Propylene glycol .....                | 20                |
| Triethanolamine .....                 | 5                 |
| Sodium lauryl sulfate .....           | 48.5              |
| Water .....                           | 16.8              |

90% of the above concentrate may be pressurized with a 60/40 mixture of propellents 114/12 at 10% concentration. If desired, a small amount from about 0.2 to 0.5% by weight of polyvinyl pyrrolidone may be incorporated in the shampoo so that in addition to functioning as a shampoo, it will also serve as a grooming agent by permitting curl retention.

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## EXAMPLE XXVII

## Nail polish remover

The solvent mixture has the following composition:

|                                       | Percent by weight |
|---------------------------------------|-------------------|
| Butyrolactone .....                   | 30                |
| Ethylene glycol monomethylether ..... | 50                |
| Ethylene glycol monobutylether .....  | 10                |
| Diethyl glycol .....                  | 5                 |
| Alkylated polymer of Example VI ..... | 5                 |

The solvent mixture was adjusted to a pH of approximately 8.0-8.5% with caustic soda to insure stability. If desired, perfume to further enhance the product may be added to the mixed solvents.

## EXAMPLE XXVIII

## Cuticle softener

|  | Percent by weight |
|--|-------------------|
| Stearyl alcohol .....                  | 22.0              |
| Cetyl alcohol .....                    | 22.0              |
| Alkylated polymer of Example VII ..... | 50.0              |
| Triethanolamine .....                  | 2.0               |
| Propylene glycol .....                 | 4.0               |

The first three components were gently heated until a clear solution was obtained. To the solution the last two components were added with stirring and allowed to cool to room temperature.

## EXAMPLE XXIX

## Bath talc

One gram of alkylated polymer of Example I was dissolved in 250 grams of hot ethanol. While maintaining the ethanol solution hot, 50 grams of talcum powder were added slowly with constant agitation. After the addition of the talc was complete, the slurry was permitted to cool to room temperature, a few drops of perfume added with mixing, and the slurry filtered, dried and the small lumpy particles broken by milling in a hammer mill. The dried fine powder was passed through the customary talc sieve and stored in a container. The alcohol may also be removed by vacuum distillation of the slurry while maintaining good agitation.

## EXAMPLE XXX

## After-shave lotion

|                                      | Percent by weight |
|--------------------------------------|-------------------|
| Alkylated polymer of Example 1 ..... | 0.1               |
| Ethanol .....                        | 99.4              |
| Lilac perfume .....                  | 0.5               |

The ethanol was heated to about the boil and the alkylated polymer added slowly until dissolved. The homogeneous cloudy solution was allowed to cool with agitation and the perfume added when the solution reached room temperature. 60% by weight of the resulting concentrate was charged in the conventional manner with 40 parts by weight of a mixture consisting of 30% by weight of propellant 12 and 10% by weight of propellant 114. The aerosol preparation was clear in view of the higher solubility of the alkylated polymer in the propellant mixture.

## EXAMPLE XXXI

## Hair spray

|                                      | Percent by weight |
|--------------------------------------|-------------------|
| Ethanol SDA-40 anhydrous .....       | 200.0             |
| Alkylated polymer of Example I ..... | 0.2               |
| Myristyl alcohol .....               | 0.2               |

The components were heated to the boil of ethanol, 5 grams of polyvinylpyrrolidone K-30 added with stirring, quickly cooled to room temperature, perfume added and 30% by weight of the cooled solution pressurized in the conventional manner with 70% by weight of a mixture

of propellents containing 35% by weight of propellant 12 and 65% by weight of propellant 11.

In this spray the alkylated polymer also functions as plasticizer for the polyvinylpyrrolidone (or copolymers thereof with vinyl acetate) and as water repellent for the film. It imparts softness and lubricity to the hair. It also reduces the tack when the polymeric film former concentration is around 5% by weight or higher in the hair spray composition.

#### EXAMPLE XXXII

##### Oil-free hair groom (gel)

0.5 gram of polyacrylic acid were dissolved in 90 grams of water at room temperature. The pH was adjusted to 7.0 with concentrated ammonium hydroxide. 5.2 grams of 45% aqueous solution of polyvinylpyrrolidone K-30 were added with moderate agitation until a homogeneous gel was obtained.

3.8 grams of polyethylene glycol having a molecular weight of 550 were melted and 0.5 gram of the alkylated polymer of Example I added with gentle heating until a solution was obtained. The resulting solution and one drop of geranium perfume were blended with the gel until a homogenous gel was obtained.

#### EXAMPLE XXXIII

##### Waterless hand cleaner (gel)

|   | Percent by weight |
|---|-------------------|
| Bayol 50 mineral oil (highly refined white mineral oil) ----- | 50.0              |
| Solution of alkylated polymer of Example XI ----              | 8.0               |
| Nonylphenol ethoxylated with 3 moles of ethylene oxide -----  | 12.0              |

The mixture was gently heated until a clear solution was obtained. To the resulting oil phase was added 30% by weight of water containing 0.25% by weight of potassium hydroxide with stirring until gelled.

This cleaner is useful for removing heavily embedded grime, oil, grease and stains.

#### EXAMPLE XXXIV

##### Dentifrice

|                                      | Percent by weight |
|--------------------------------------|-------------------|
| Calcium carbonate -----              | 51.3              |
| Alkylated polymer of Example I ----- | 0.5               |
| Sodium lauryl sulfoacetate -----     | 2.1               |
| Glycerine -----                      | 28.7              |
| Water -----                          | 17.4              |
| Gum and flavor -----                 | q.s.              |

The calcium carbonate was mixed with the water and glycerine to yield a uniform suspension. To the suspension was added in sufficient quantity the customary gum and peppermint flavor to yield a paste. The alkylated polymer was mixed with the sodium lauryl sulfoacetate and incorporated into the paste with thorough mixing.

#### EXAMPLE XXXV

The preparation of the paste rouge of Example XXI was repeated with the exception that the oil solution of alkylated polymer of Example VIII was replaced by the same amount of the oil solution of the alkylated polymer of Example XII.

From Examples XIII to XXXV it is evident that the alkylated polymers (homopolymers and copolymers) of heterocyclic N-vinyl monomers are not only soluble in, but also compatible with, a large variety of currently used and acceptable toiletry carriers (cosmetics and soaps) to yield compositions having new, novel and desirable properties.

Because of their softening and soothing effects, the alkylated polymers may be employed in the preparation of pharmaceutical salves, ointments and suppositories. Such preparations may contain the usual antiseptic, germicidal and medicinal agents.

The alkylated polymers display their desirable emollient effects in all types of ointments, salves, lotions, antiseptics, disinfectants, and other medicinal preparations for external use. The alkylated polymers are especially adaptable in the preparation of non-irritating detergent emulsions as skin cleansers for removing grease and oils from the skin. They manifest their softening and soothing effects when incorporated in hemorrhoidal preparations. They can be incorporated into unctuous materials and employed as lubricants to aid the passage of catheters or enema tubes. They can be incorporated into salves and ointments used in the treatment of burns. Due to the water insolubility of the alkylated polymers, a continued softening (emollient) effect is noted even after several washings of the skin with soap and water.

While the present specification has shown the new and useful application of a large class of alkylated polymers of heterocyclic N-vinyl monomers in cosmetics and soaps, alkylated polymers (homo- and co-polymers) of other heterocyclic N-vinyl monomers containing a



group in the ring may be employed as additives in accordance with the present invention. Such monomers include the N-vinyl monomers of alkyl substituted derivatives of lactams such as, for example, 4,4-dimethyl-2-pyrrolidone, 3,3-dimethyl-2-pyrrolidone, 3-ethyl-2-pyrrolidone, 3,5-dimethyl-2-pyrrolidone, 3-ethyl-2-pyrrolidone, 4-acryl-2-pyrrolidone, 5-ethyl-2-pyrrolidone, 3-methyl-2-pyrrolidone, 4-methyl-2-pyrrolidone, 3,3,5-trimethyl-2-pyrrolidone, 5,5-diethyl-2-piperidone, 5,6-dimethyl-2-piperidone, 4-ethyl-2-piperidone, 6-ethyl-3-methyl-2-piperidone, 3-methyl-2-piperidone, 4-methyl-2-piperidone, 5-methyl-2-piperidone, 3,6-dimethyl-2-caprolactam, 4,6-dimethyl-2-caprolactam, 4,7-dimethyl-2-caprolactam, 7,7-diethyl-2-caprolactam, 3-ethyl-2-caprolactam, 5-ethyl-2-caprolactam, 6-ethyl-2-caprolactam, 4-ethyl-6-methyl-2-caprolactam, 6-methyl-2-caprolactam, 6-ethyl-4-methyl-2-caprolactam, 3-methyl-2-caprolactam, 4-methyl-2-caprolactam, 5-methyl-2-caprolactam; 6-methyl-2-caprolactam; N-vinyl monomers of 3,5-dimethyl-3-morpholinone, 2-oxazinidinone (U.S. Patent 2,905,660 and U.S. Patent 3,097,087), 5-ethyl-2-oxazinidinone, 5-phenyl-2-oxazinidinone, 4,5-dimethyl-2-oxazinidinone, 5,5-dimethyl-2-oxazinidinone, 2,5-diphenyl-2-oxazinidinone, 2-phenyl-4-oxothiazolidone, 2,2'-diphenyl-4-oxothiazolidone, 2,2'-dimethyl-4-oxothiazolidone, 2-oxazolidinone (U.S. Patent 2,905,690 and U.S. Patent 2,891,058), 5-methyl-2-oxazolidinone, 4-methyl-2-oxazolidinone, 5-ethyl-2-oxazolidinone, 4,5-dimethyl-2-oxazolidinone, 2-phenyl-2-oxazolidinone, 5-butyl-2-oxazolidinone, 5-propyl-2-oxazolidinone, 4,5-diethyl-2-oxazolidinone, 2-piperazonone (JACS 62, 1202 (1940)), 3,3-dimethyl-2-ketopiperazine and 3-methyl-2-ketopiperazine, 4-thiazolidone (JACS 76, 578 (1954)), 2-thiazolidone (J. Chem. Soc. 1949, 2367), 2-methyl-4-thiazolidinone, 2-phenyl-4-thiazolidinone dioxide, 3-thiamorpholinone, 2-pyrimidone (J. Chem. Soc. 1959, 525), 2-imidazolidones (e.g. Ann. 232, 227 (1886)), N,N-ethylenethioureas (J. Biol. Chem. 163, 761 (1946)); tetrahydro-(2H, 1,3)-oxazin-3-ones (U.S. Patent 2,940,971), and the like.

In preparing alkylated polymers (homo- and copolymers) of the foregoing N-vinyl monomers, it is preferred to follow the simultaneous polymerization and alkylation procedure described in the aforementioned application of Merijan and Grosser, Serial No. 358,406 while adhering to the proportions of co-reactants described herein.

By the term "skin," as employed in the following claims, is meant skin in general, which is the external covering or integument of the body and includes the scalp which is an integument of the upper part of the head. Since hair is the natural covering of the head growing from the skin and since nails (modified epidermis,



skin) grow on the upper side of the ends of fingers and toes, the term "appendages of the skin" includes hair and nails.

We claim:

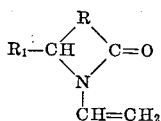
1. A composition for application to a member of the group consisting of skin and appendages of the skin containing as an essential component in a toiletry carrier from 0.1 to about 50% by weight of said carrier of an alkylated polymer of an N-vinyl heterocyclic monomer wherein on an average of at least 25% of the N-vinyl heterocyclic monomer units in said polymer are alkylated with an alkyl chain of from 10 to 42 carbon atoms, said alkylated polymer being selected from the class consisting of polymers prepared by

(a) the simultaneous polymerization and alkylation of one mole of a monomer selected from the group consisting of at least one N-vinyl heterocyclic monomer and a mixture of monomers containing from 60 to 95% by weight of said N-vinyl heterocyclic monomer and from 5% to 40% by weight of a non-heterocyclic polymerizable monoethylenically unsaturated monomer, and

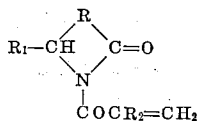
(b) by the alkylation of one mole of a polymer selected from the group consisting of homopolymer of said N-vinyl heterocyclic monomer and copolymer of said N-vinyl heterocyclic monomer and said non-heterocyclic polymerizable monoethylenically unsaturated monomer,

with 0.5 to 4 moles of an alpha-olefin of from 10 to 42 carbon atoms in solution of an organic solvent common to said selected monomer, mixture of monomers, homopolymer and copolymer, and alpha-olefin in the presence of 0.025 to 0.30 mole of an organic peroxide catalyst per mole of said alpha-olefin at a temperature ranging from 100 to 200° C., said heterocyclic N-vinyl monomer is selected from the class consisting of N-vinyl succinimide, N-vinyl diglycolylamide, N-vinyl glutaramide, N-vinyl 3-morpholinone, N-vinyl 5-methyl-3-morpholinone, N-vinyl 5-ethyl-3-morpholinone and monomers of the following formulae:

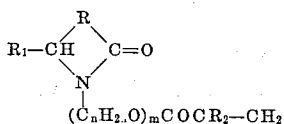
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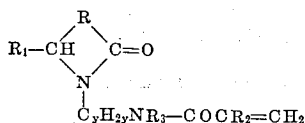
(2)



(3)



(4)



wherein R represents an alkylene bridge of from 2 to 4 carbon atoms to complete a 5-, 6- and 7-membered heterocyclic ring system, R<sub>1</sub> represents a member selected from the class consisting of hydrogen, methyl and ethyl, R<sub>2</sub> represents a member selected from the class consisting of hydrogen and methyl, R<sub>3</sub> represents a member selected from the class consisting of hydrogen, alkyl of from 1 to 12 carbon atoms and phenyl, m is an integer of from 1 to 4, n is an integer of from 1 to 4 when m has a value of 1, and from 2 to 4 when m has a value greater than 1, and y is an integer of from 2 to 3, and the said non-heterocyclic polymerizable monoethylenically unsaturated monomer is selected from the class consisting

of vinyl esters, vinyl chloride, vinylidene chloride, acrylonitrile, styrene, acrylic acid, acrylate esters, methacrylic acid, methacrylate esters, methacrylonitrile, acrylamides and methacrylamides.

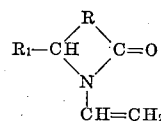
2. A composition for application to a member of the group consisting of skin and appendages of the skin containing as an essential component in a toiletry carrier from 0.1 to about 50% by weight of said carrier of an alkylated polymer of an N-vinyl lactam monomer wherein on an average of at least 25% of the N-vinyl lactam monomer units in said polymer are alkylated with an alkyl chain of from 10 to 42 carbon atoms, said alkylated polymer being selected from the class consisting of polymers prepared by

(a) the simultaneous polymerization and alkylation of one mole of a monomer selected from the class consisting of at least one N-vinyl lactam monomer and a mixture of monomers containing from 60 to 95% by weight of said N-vinyl lactam monomer and from 5% to 40% by weight of a non-heterocyclic polymerizable monoethylenically unsaturated monomer, and

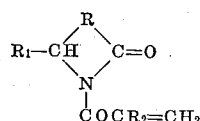
(b) by the alkylation of one mole of a polymer selected from the group consisting of homopolymer of said N-vinyl lactam monomer and copolymer of said N-vinyl lactam monomer and said non-heterocyclic polymerizable monoethylenically unsaturated monomer,

with 0.5 to 4 moles of an alpha-olefin of from 10 to 42 carbon atoms in solution of an organic solvent common to said selected monomer, mixture of monomers, homopolymer, copolymer and alpha-olefin in the presence of 0.025 to 0.30 mole of an organic peroxide catalyst per mole of said alpha-olefin at a temperature ranging from 100 to 200° C., and said N-vinyl lactam monomer is selected from the class consisting of monomers of the following formulae:

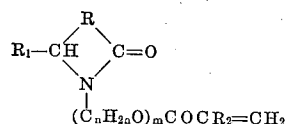
(1)



(2)

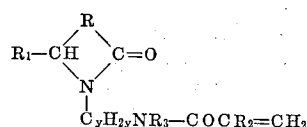


(3)



and

(4)



wherein R represents an alkylene bridge of from 2 to 4 carbon atoms to complete a 5-, 6- and 7-membered heterocyclic ring system, R<sub>1</sub> represents a member selected from the class consisting of hydrogen, methyl and ethyl, R<sub>2</sub> represents a member selected from the class consisting of hydrogen and methyl, R<sub>3</sub> represents a member selected from the class consisting of hydrogen, alkyl of from 1 to 12 carbon atoms and phenyl, m is an integer of from 1 to 4, n is an integer of from 1 to 4 when m has a value of 1, and from 2 to 4 when m has a value greater than 1, and y is an integer of from 2 to 3, and the said non-heterocyclic polymerizable monoethylenically unsaturated monomer is selected from the class consisting of vinyl esters, vinyl chloride, vinylidene chloride, acrylonitrile, styrene, acrylic acid, acrylate esters,

methacrylic acid, methacrylate esters, methacrylonitrile, acrylamides and methacrylamides.

3. A cosmetic cream for softening and soothing the skin containing as an essential component in a dermatologically acceptable carrier from 0.1% to about 50% by weight of said carrier of an alkylated polymer of an N-vinyl heterocyclic monomer prepared by the process defined in claim 1.

4. A soap for conditioning and softening the skin containing as an essential component in a dermatologically acceptable carrier from 0.1% to about 50% by weight of said carrier of an alkylated polymer of an N-vinyl heterocyclic monomer prepared by the process defined in claim 1.

5. A lotion for conditioning and softening the skin containing as an essential component in a dermatologically acceptable carrier from 0.1% to about 50% by weight of said carrier of an alkylated polymer of an N-vinyl heterocyclic monomer prepared by the process defined in claim 1.

6. A cuticle softener for conditioning and softening the cuticles of the nails of fingers and toes containing as an essential component in a dermatologically acceptable carrier from 0.1% to about 50% by weight of said carrier of an alkylated polymer of an N-vinyl heterocyclic monomer prepared by the process defined in claim 1.

7. A hair grooming composition for imparting softness, lubricity, lustre and manageability to the hair containing as an essential component in a dermatologically acceptable carrier from 0.1% to about 50% by weight of said carrier of an alkylated polymer of an N-vinyl heterocyclic monomer prepared by the process defined in claim 1.

8. A toiletry preparation for application to a member selected from the group consisting of skin and appendages of the skin containing as an essential component in a toiletry carrier from 0.1% to about 50% by weight of said carrier of an alkylated homopolymer of N-vinyl-2-pyrrolidone, wherein on the average of at least 50% of the N-vinyl-2-pyrrolidone units in said homopolymer are alkylated with an alkyl group of from 10 to 42 carbon atoms, prepared by the alkylation of one mole of the homopolymer of N-vinyl-2-pyrrolidone with 0.5 to 4 moles of an  $\alpha$ -olefin of from 10 to 42 carbon atoms in solution of an organic solvent common to said homopolymer and  $\alpha$ -olefin in the presence of 0.25 to 0.3 mole of an organic peroxide catalyst per mole of said  $\alpha$ -olefin at a temperature ranging from 100° to 200° C.

9. A toiletry preparation for application to a member selected from the group consisting of skin and appendages of the skin containing as an essential component in a toiletry carrier from 0.1% to about 50% by weight of said carrier of an alkylated homopolymer of N-vinyl-5-methyl-2-pyrrolidone, wherein on the average of at least 50% of the N-vinyl-5-methyl-2-pyrrolidone units in said homopolymer are alkylated with an alkyl group of from 10 to 42 carbon atoms, prepared by the alkylation of one mole of the homopolymer of N-vinyl-5-methyl-2-pyrrolidone with 0.5 to 4 moles of an  $\alpha$ -olefin of from 10 to 42 carbon atoms in solution of an organic solvent common to said homopolymer and  $\alpha$ -olefin in the presence of 0.025 to 0.3 mole of an organic peroxide catalyst per mole of said  $\alpha$ -olefin at a temperature ranging from 100° to 200° C.

ide catalyst per mole of said  $\alpha$ -olefin at a temperature ranging from 100° to 200° C.

10. A toiletry preparation for application to a member selected from the group consisting of skin and appendages of the skin containing as an essential component in a toiletry carrier from 0.1% to about 50% by weight of said carrier of an alkylated homopolymer of N-vinyl-piperidone, wherein on the average of at least 50% of the N-vinyl-piperidone units in said homopolymer are alkylated with an alkyl group of from 10 to 42 carbon atoms, prepared by the alkylation of one mole of the homopolymer of N-vinylpiperidone with 0.5 to 4 moles of an  $\alpha$ -olefin of from 10 to 42 carbon atoms in solution of an organic solvent common to said homopolymer and  $\alpha$ -olefin in the presence of 0.025 to 0.3 mole of an organic peroxide catalyst per mole of said  $\alpha$ -olefin at a temperature ranging from 100° to 200° C.

11. A toiletry preparation for application to a member selected from the group consisting of skin and appendages of the skin containing as an essential component in a toiletry carrier from 0.1% to about 50% by weight of said carrier of an alkylated homopolymer of N-vinyl- $\epsilon$ -caprolactam, wherein on the average of at least 50% of the N-vinyl- $\epsilon$ -caprolactam units in said homopolymer are alkylated with an alkyl group of from 10 to 42 carbon atoms, prepared by the alkylation of one mole of the homopolymer of N-vinyl- $\epsilon$ -caprolactam with 0.5 to 4 moles of an  $\alpha$ -olefin of from 10 to 42 carbon atoms in solution of an organic solvent common to said homopolymer and  $\alpha$ -olefin in the presence of 0.025 to 0.3 mole of an organic peroxide catalyst per mole of said  $\alpha$ -olefin at a temperature ranging from 100° to 200° C.

12. A toiletry preparation for application to a member selected from the group consisting of skin and appendages of the skin containing as an essential component in a toiletry carrier from 0.1% to about 50% by weight of said carrier of an alkylated homopolymer of N-vinyl-2-pyrrolidone, wherein on the average of at least 50% of the N-vinyl-2-pyrrolidone units in said homopolymer are alkylated with an alkyl group of from 10 to 42 carbon atoms, prepared by the simultaneous polymerization and alkylation of one mole of N-vinyl-2-pyrrolidone with 0.5 to 4 moles of an  $\alpha$ -olefin of from 10 to 42 carbon atoms in solution of an organic solvent common to said pyrrolidone and  $\alpha$ -olefin in the presence of 0.025 to 0.3 mole of an organic peroxide catalyst per mole of said  $\alpha$ -olefin at a temperature ranging from 100° to 200° C.

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