Research Report

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Project Title: Conditioning Shampoo

Section/Section Manager: Shampoos / M. W. Parslow

Author(s): R. Y. LOCHHEAD

Ext.Ref: P IS 79 1153

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Report Title: FORMULATION OF AN ANTIDANDRUFF SHAMPOO WITH IMPROVED HAIR CONDITIONING ATTRIBUTES.

Project No: H01

IMIS No: 14 02 10 260

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Objective

To develop a Zinc PTO containing anti-dandruff shampoo which possesses improved hair conditioning attributes derived from utilisation of the Jaguar/ Briphos technology.

Nature and Scope of the Study

Following a company brief, an attempt was made to simultaneously incorporate Jaguar C-13-S and Briphos 03D, as conditioning agents, into a Zinc-PTO-containing anti-dandruff shampoo. In order to achieve this it was essential to omit the clay suspending agent from the existing formulation because interaction between the polymeric cationic conditioning agent and the clay would be likely to lead to instability of the shampoo with respect to separation and sedimentation of the Zinc PTO particles.

A stable product has been formulated and possible reasons for this stability have been advanced.

Conclusions

1. A conditioning variant of anti-dandruff shampoo containing Zinc PTO has been developed.

2. Laboratory prepared versions of this formulated product are stable against sedimentation and separation after three months storage.

3. The formulated product is equivalent to prototype 95C and superior to "Head and Shoulders", and "All Clear" dry variant for wet combing properties measured in vitro.

4. The product is equivalent to 95C and superior to "Head and Shoulders" and "All Clear" dry variant at the 5% significance level for the attributes Feel, Dry-Combing, and Static, by in vitro assessment.

5. "Head and Shoulders", "95C", "All Clear" dry variant, and the product described here are all equivalent, at the 5% significance level, for gloss, by in vitro assessment.

6. "Head and Shoulders" is superior to the formulated product described here, at the 5% significance level, for "amount of lather" and "creaminess of lather" by in vitro assessment.

Limitations

This development has been conducted on a laboratory scale and the conditioning properties have only been established in vitro.

Further work will be necessary to obtain safety, conduct salon and consumer trials, assess deposition efficiency, anti-dandruff effectiveness and establish technology limitations.

INTRODUCTION

A recent company brief (1) requested the development of an anti-dandruff shampoo having shampoo attributes comparable to New Sunsilk Dry.

New Sunsilk Dry is based on the URLI conditioning shampoo 95C (2) using sodium lauryl ether sulphate and having the quaternised guar gum derivative, Jaguar C-13-S, and the phosphate ester, Briphos 03D, as conditioning additives.

The current dry variant anti-dandruff shampoo, "All Clear", contains Briphos 03D. Therefore the problem was reduced to finding a suitable means of incorporating Jaguar C-13-S into a sodium lauryl ether sulphate-based shampoo with Zinc-pyridine-2-thiol-N-oxide added as the active anti-dandruff ingredient.

Definition of the Problem

Zinc pyridine-2-thiol-N-oxide (Zinc PTO) is a finely divided powder of specific gravity 1.782 and average particle size of the order of 5 microns and smaller. The material is supplied as a 48 per cent slurry in water, with some nonionic detergent added to prevent irreversible flocculation.

As a consequence of its relatively high density Zinc PTO has a tendency to sediment from most normal shampoo formulations. This sedimentation may be retarded by simply increasing the viscosity of the shampoo, when the sedimentation rate would decrease in accordance with Stokes Law. However, in order to formulate a product with acceptable stability against separation a Brookfield viscosity of at least 3500 cps would have to be attained (3). Such a product would have the consistency of a cream rather than the normal lotion characteristics associated with shampoos.

Stable Zinc-PTO-containing shampoos having a more normal lotion-viscosity can be produced by including a suspending agent in the formulation. It is essential that the suspending agent in the formulation adopts a network structure which extends throughout the product. This network structure must break down easily when sheared in order that the product may exhibit liquid-like flow, but the structure must be capable of reforming reasonably quickly in order that minimal sedimentation of the Zinc PTO occurs following shearing of the product. Most thixotropic systems do not recover quickly enough to meet this requirement. Rheologically the desired behaviour is described as shear-thinning and in order to suspend effectively at low shear the product must exhibit a yield point. At shear stresses below the yield stress the product will behave as a solid and at shear stresses in excess of the yield stress liquid like behaviour will be observed. Clearly the ideal product yield stress will have a value higher than that exerted by the gravitational pull on the Zinc PTO particles, but lower than that exerted in normal pouring and filling operations.

In existing anti-dandruff shampoos containing Zinc PTO modified clays, such as Laponite, are used as suspending agents. Modified hectorite clays appear to be preferred - Veegum in Procter and Gamble's "Head and Shoulders" and Propaloid T in our concern product "All Clear".

The apparently obvious route to a conditioning, anti-dandruff shampoo is to add Jaguar C-13-S to the existing hectorite-clay-stabilised shampoo. It has been reported, however, that cationic, polymeric conditioning agents cannot be used with Veegum or Laponite (2). The cationic polyelectrolytes probably cause extensive flocculation of the clay structure, which would simultaneously cause a loss of the attributes connected with the polymer and also with the clay structure.

This problem was obviously appreciated by the Procter and Gamble Company (11) for in their British Patent 1,195,158 they show, in particular, two examples of formulae containing the cationic cellulose ether, Polymer JR. In both cases (Examples I and II in the Patent Specification) the clay has been omitted and the detergents themselves have been structured - in the first case by adding relatively large amounts of sodium chloride and sodium sulphate and in the second case by having a formula based essentially on 10 per cent lauryl sulphate and 10 per cent coconut alkyl dimethyl amine oxide. This latter formula is similar to Unilever's "Jif" suspending base.

The Solution

Many polysaccharides form gels in association with water. This behaviour may be attributed to the molecular structure of these polysaccharides which consist of long chain molecules having long freely soluble sequences of segments interlinked with a series of sites which are capable of intermolecular aggregation. The gel is formed with water by a network of the soluble sequences of the chains cross-linked at the aggregation sites (4-6).

Jaguar C-13-S is a quaternary nitrogen substituted guar gum. Guar gum is predominantly composed of the galactomannan polysaccharide, guaran.

If Jaguar C-13-S could be induced to form a cross-linked network throughout the shampoo then this network could possibly be capable of suspending Zinc PTO. In this way the problematic clay could be omitted from the formulation and the polymeric cationic conditioning agent could be included in the formulation at one and the same time. Unquaternised Guar gum, however, is characteristically very water soluble; it tends to dissolve in water to give viscous polymeric solutions rather than gels (6, 8). Quaternisation would tend to make such a material even more water-soluble and less likely to form gels.

The galactomannans, generally, consist of a B-D-(1,4) mannan backbone having α-D-(1,6)- linked galactose branches. In some galectomannans, e.g. locust bean gum, the galactose substituents are clustered predominantly in long blocks of around 25 residues interspersed by even longer regions of essentially unsubstituted mannan backbone (7) illustrated schematically in Figure 1. The highly branched portions of this polysaccharide are highly soluble and the unsubstituted portions tend to aggregate (Fig. 2). Therefore, locust bean gives gels in water.

Guar gum, on the other hand, is much more highly substituted with galactose and it appears that the galactose side units are distributed relatively evenly along the chain, leaving very few unsubstituted "runs" of B-D-(1,4)- mannan. Clearly, the opportunity for cross-links to form is severely limited by the absence of unsubstituted backbone and this, therefore, explains why guar gum tends to give viscous solutions rather than gels. If cross-link sites could be introduced into guar gum, then owing to its very high intrinsic solubility, excellent gels which would not exhibit syneresis even at very low concentrations would be expected. Furthermore, if the cross-links were non-covalent then transient bonds which would be reformed after cleavage could result. Such characteristics would give a shear-thinning gel with the right properties to be a shampoo-suspending agent.

The quaternised guar gum derivative, Jaguar C-13-S, interacts strongly with anionic surfactants (9). This interaction is often depicted schematically as a pure ion-pair bond, although for such a hydrophilic polymer a more accurate picture may be entrapment of the cationic polymer within the electrical double layer of the micelle - with, perhaps, a consequent change in micelle size and shape. Whichever model is accepted makes little difference to the following argument which speculates on the possibility of networks being formed within shampoo systems based on anionic detergents and containing Jaguar C-13-S.

At normal neat shampoo concentrations most of the anionic surfactant present will be in the form of micelles. It is conceivable that any of these micelles could interact with more than one molecular chain of Jaguar C-13-S. In such a situation the micelle itself would constitute a cross-link between the chains. In this way Jaguar C-13-S and the micelles could build a network throughout the whole of the shampoo. The micelles have the additional advantageous property of existing in dynamic equilibrium with the free monomeric surfactant and they are, therefore, continually being broken down and reformed at very rapid rates of the order of fractions of a second (9). Thus, the Jaguar C-13-S micelle interaction could lead to a dynamic network which would continually change at the molecular level but would maintain an average network integrity over distances larger than molecular sizes. Such a network would have exactly the correct shear-thinning, rapid "healing" properties required of a suspending agent and if this was the case the Jaguar C-13-S anionic surfacant shampoo system alone might be capable of suspending Zinc PTO particles.

All of the above is, of course, reasoned speculation and it is essential that this model be tested experimentally in order to assess the feasibility of this approach.

RESULTS

Zinc PTO was included in two formulations (Appendices I and II) which, apart from colour and perfume, were essentially the same as 95C* with Jaguar/Briphos conditioning additives.

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* Jaguar/Briphos Conditioning Shampoo - S.J.Sime. P IS 79 1029.

Stability

Samples of the shampoos were placed in storage at temperatures of 0°, 15°, 28°, 37°, and 50°C. After three months' storage slight separation of the samples at 0°C and 50°C had occurred, but all of the other samples appeared to be stable against separation and sedimentation of the Zinc PTO.

A second batch of shampoo prepared one month later showed gross separation at 0°C, but was essentially similar to the previous batch at all other temperatures. These results represent acceptable stability.

If the stability arises from structuring of the system, then the system should exhibit a yield stress. The yield stress required for suspension of the particles can be calculated using Archimedes' Principle.

Thus assuming a particle size of 5 microns and a density difference of 0.78 g/cc -

Force downwards = $^4/_3 \pi (5 \times 10^{-4})^3 \times (0.78) \times 981$ dynes.

If it is assumed that this force is exerted on an area of "liquid" corresponding to the circle having the same radius as the spherical particle, then:

$$\text{Minimum yield stress for suspension} = \frac{^4/_3 \pi (5\times10^{-4})^3 \times 0.78 \times 981}{\pi (5\times10^{-4})^2} \text{ dynes/cm}^2$$

$$= \underline{\underline{0.51 \text{ dynes cm}^{-2}}}$$

The rheological characteristics were measured using a Deer Rheometer. No yield stress was found, but the value of 0.51 dynes cm^{-2} is below the limit of measurement for the Deer Rheometer.

The lower limit of measurement of the instrument used was 0.9 dynes cm^{-2}. Since the formulations were stable against sedimentation we, therefore, conclude that the system had yield stress below the level of measurement by our existing techniques but still adequate for the purpose of suspending Zinc PTO.

The traditional Zinc PTO-containing anti-dandruff shampoo stabilised by clay (Propaloid T) also had no measureable yield stress.

Shampoo Attributes

The two new conditioning anti-dandruff formulations were tested "in vitro" for shampoo and conditioning attributes against the existing clay-stabilised dry variant of "All Clear", Procter and Gamble's "Head and Shoulders", and 95C* (with Jaguar/Briphos).

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* Jaguar/Briphos Conditioning Shampoo - S.J.Sime. P IS 79 1029.

Wet Combing

The T.C.T. method of wet combing was employed (12). Figures refer to the mean of three switches.

System	% Remaining Relative to 16% MLS Base
Head and Shoulders	59.8
"All Clear" Dry Variant	90.5
95C*	24.2
Test Formulation I	19.9
Test Formulation II	12.5

Thus "in vitro" testing indicates that the new formulations are superior to the competitor's product (Head and Shoulders), the existing product ("All Clear") and comparable to the action standard 95C.

The remaining attributes were analysed by Duncan's Multiple Range Test at the 5% level. Products connected by underlining are not significantly different at the 5% level: (most favourable product on left).

GLOSS

FORMULATION II HEAD & SHOULDERS FORMULATION I NEW SUNSILK DRY ALL CLEAR

There was no significant difference between the products for Gloss

FEEL

FORMULATION II FORMULATION I 95C HEAD & SHOULDERS ALL CLEAR

DRY COMBING

FORMULATION II FORMULATION I 95C HEAD & SHOULDERS ALL CLEAR

STATIC

FORMULATION II FORMULATION I 95C HEAD & SHOULDERS ALL CLEAR

CREAMINESS OF LATHER

HEAD & SHOULDERS	FORMULATION I	FORMULATION II

AMOUNT OF LATHER

HEAD & SHOULDERS	FORMULATION I	FORMULATION II

CONCLUSIONS

1. A conditioning variant of anti-dandruff shampoo containing Zinc PTO has been developed.

2. This formulated product is stable against sedimentation and separation.

3. The formulated product is superior to "95C", "Head and Shoulders", and "All Clear" dry variant, for Wet Combing.

4. The product is equivalent to "95C" and superior to "Head and Shoulders" and "All Clear" dry variant at the 5% significance level for the attributes Feel, Dry-Combing and Static.

5. "Head and Shoulders", 95C, "All Clear" dry variant, and the product described here are all equivalent, at the 5% significance level, for gloss.

6. "Head and Shoulders" is superior to the formulated product described here, at the 5% significance level, for "amount of lather" and "creaminess of lather".

ACKNOWLEDGEMENTS

I would like to acknowledge the assistance of Mr. J. Britzman in conducting the experimental work and express my thanks to Dr.R.Donaldson and Dr.D.Hall of U.R.L.Port Sunlight and Dr.E.R.Morris of U.R.L.Colworth House for their helpful discussions.

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R.Y.Lochhead

RYL/NJH
30th October 1979

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12.	TRM 10916		Wet combing resistance measurement - a new test method for in vitro screening - current status.	J.K.Prall

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APPENDIX

FORMULATION I

	Percentage in product	
Sodium Lauryl Ether Sulphate (2EO)	11.4	) Added as Empicol XC35J
Coconut diethanolamide	2.5	) The phosphate ester
Ethylene glycol monostearate	2.5	) in this product is
Phosphate Ester	1.5	) Briphos 03D.
Jaguar C-13-S	0.3	
Zinc-pyrithione	1.0	
Formaldehyde	0.15	
NaCl	0.33	
Zinc Sulphate heptahydrate	0.1	

pH → 6.5 - 7.00 with 1M NaOH

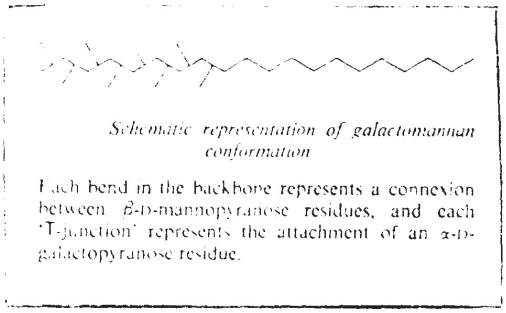
Product viscosity 1800-2000 cps

FORMULATION II

Sodium Lauryl Ether Sulphate (2EO)	11.4	) Added as Empicol XC35J
Coconut diethanolamide	2.5	)
Ethylene glycol monostearate	2.5	)
Phosphate Ester	1.5	)
Coconut diethanolamide (Empilan CDX/A)	2.00	
Jaguar C-13-S	0.3	
Zinc pyrithione	1.0	
Formaldehyde	0.15	
NaCl	0.33	
Zinc sulphate heptahydrate	0.1	

pH → 6.5 - 7.00 with IM NaOH

Product viscosity 1800-2000 cps



Schematic representation of galactomannan conformation

Each bend in the backbone represents a connexion between β-D-mannopyranose residues, and each 'T-junction' represents the attachment of an α-D-galactopyranose residue.

FIG. 1. Reproduced from D.A.Rees, Biochem J., (1972), 126, 265.

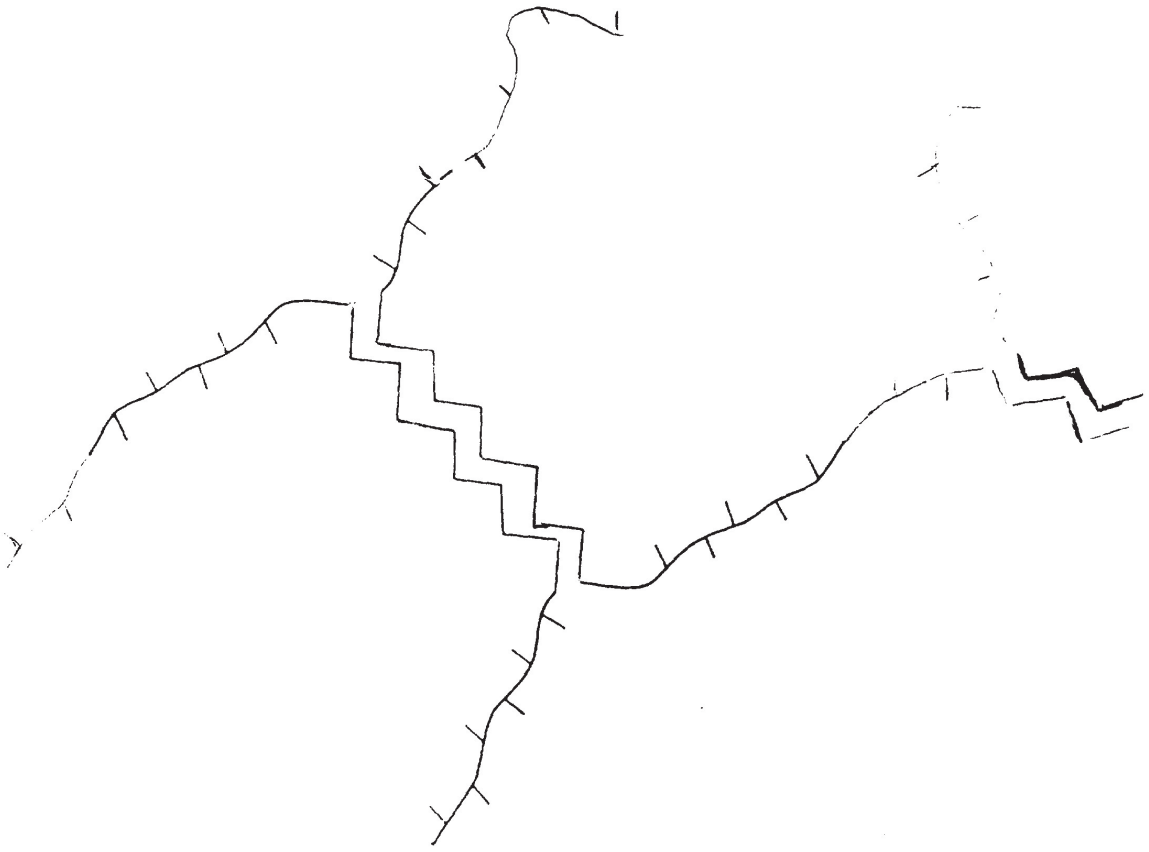


FIG. 2. Possible model for the formation of a cross-linked network by locust bean galactomannan.