

POLYVINYLPIRROLIDONE, ITS MANUFACTURE, PROPERTIES AND USE IN COSMETICS

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1. HISTORICAL NOTE

POLYVINYLPIRROLIDONE WAS first synthesised in Germany by Walter

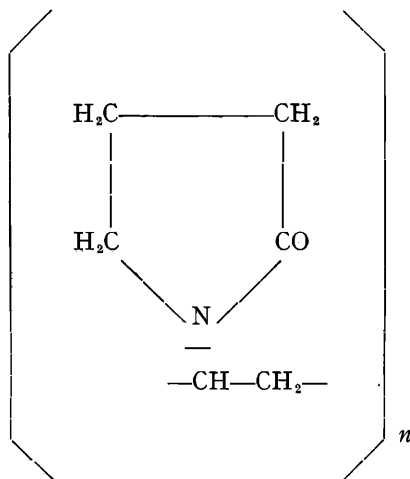


Fig. 1. Structure of Polyvinylpyrrolidone.

Reppe during the late 1930's^{1,2,3} and was initially evaluated there as a possible blood plasma substitute during World War II.⁴ It has, of course, been known for many years that hydrophilic colloids could be retained in the blood stream long enough to be suitable as replacement fluids for natural blood, and during the first World War substances such as gum arabic were used for this purpose. These early materials, although useful in an emergency, all exhibited harmful side effects, and at the beginning of World War II two German workers, Weese and Hecht, evaluated a number of the newer water-soluble colloidal high polymers with a view to developing an improved plasma substitute without the earlier defects. They finally settled on polyvinylpyrrolidone,⁴ and a plasma substitute based on this was used quite widely by the German medical services during the war, and similar materials have indeed been used subsequently in America, Europe and elsewhere.

From this initial use a number of other medical applications have been developed, and it is not surprising that uses outside the medical field have received a good deal of attention. To date, industrial uses for the polymer

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have been developed in the textile industry, photographic industry and so on. It is with one group of such uses, in the formulation of cosmetics and toilet preparations, that we are now concerned.

It should be emphasised at the outset that special grades of polyvinylpyrrolidone are required for internal medical use, and materials supplied for industrial and cosmetic purposes should not be used in pharmaceuticals.

2. SYNTHESIS

SYNTHESIS OF POLYVINYLPIRROLIDONE

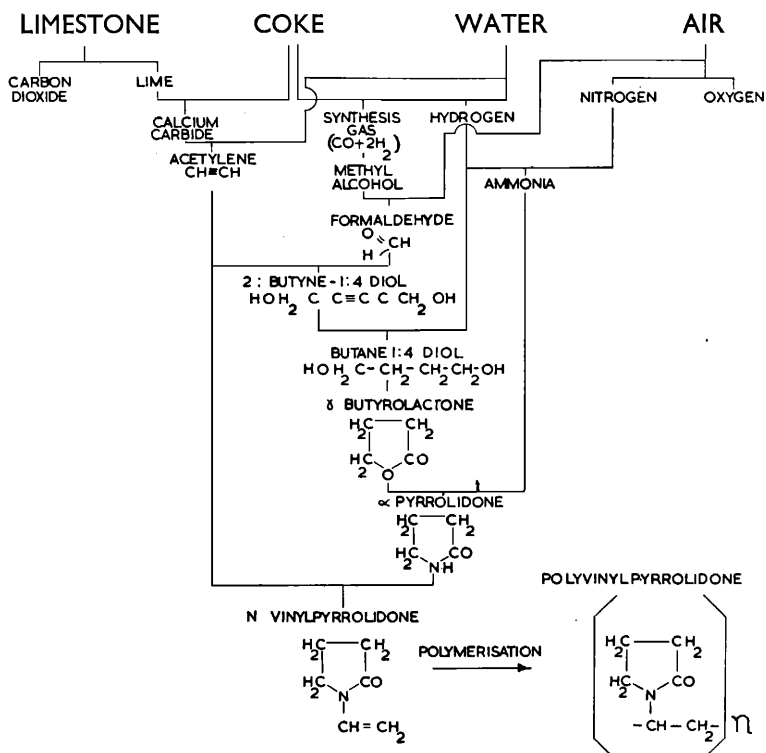


Fig. 2. Synthesis of Polyvinylpyrrolidone.

Polyvinylpyrrolidone is primarily derived from limestone, coke, water and air, and is therefore potentially available in unlimited quantities. As it is completely synthetic there is little variation in the properties or quality of the material, which can be controlled during manufacture.

The polymer is prepared by the following series of reactions, two of which involve the use of acetylene under elevated pressures.

It is perhaps worth mentioning that in handling acetylene, explosive

decompositions can readily be initiated at pressures above 0.6 atm. above atmospheric pressure, and special precautions and techniques have to be adopted to avoid the associated hazards. Indeed, such operations are governed by legislation issued under Orders in Council, which only permit the handling of acetylene at pressures up to 9 lb. per sq. inch normally ; very special precautions are called for at higher pressures. For chemical purposes, pressures up to 20 atmospheres may be used, subject to the approval by H.M. Chief Inspector of Explosives of the equipment and the techniques used. The equipment illustrated, particularly in Fig. 8, has been designed to meet these requirements. This equipment is probably amongst the most advanced in design with regard to safety existing at this time.

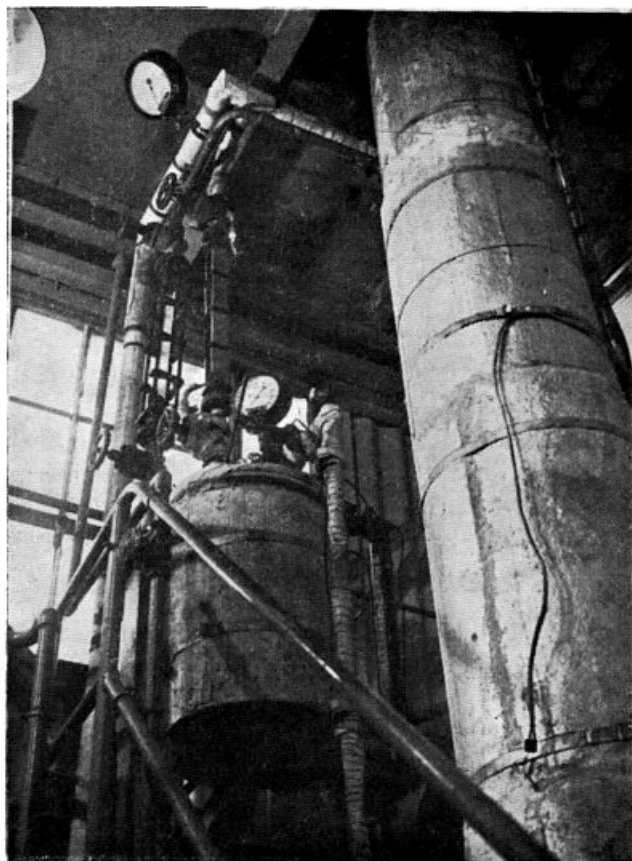


Fig. 3. View of the reactor and vessel used in the production of gamma butyrolactone.

In producing polyvinylpyrrolidone, acetylene and formaldehyde are first reacted under pressure in the presence of a suitable catalyst to prepare 2-butyne-1 : 4-diol. This is then hydrogenated to butane-1 : 4-diol, which in the presence of another catalyst is simultaneously dehydrogenated and ring closure effected to give gamma butyrolactone. This, in turn, is then reacted with ammonia under pressure to give alpha pyrrolidone, and further reaction with acetylene under pressure then gives vinyl pyrrolidone monomer.

The monomer is polymerised under carefully controlled conditions to give an aqueous solution of polyvinylpyrrolidone of the desired molecular weight. This solution can then either be sold as such or submitted to a spray-drying operation to remove the water and trace volatile impurities,

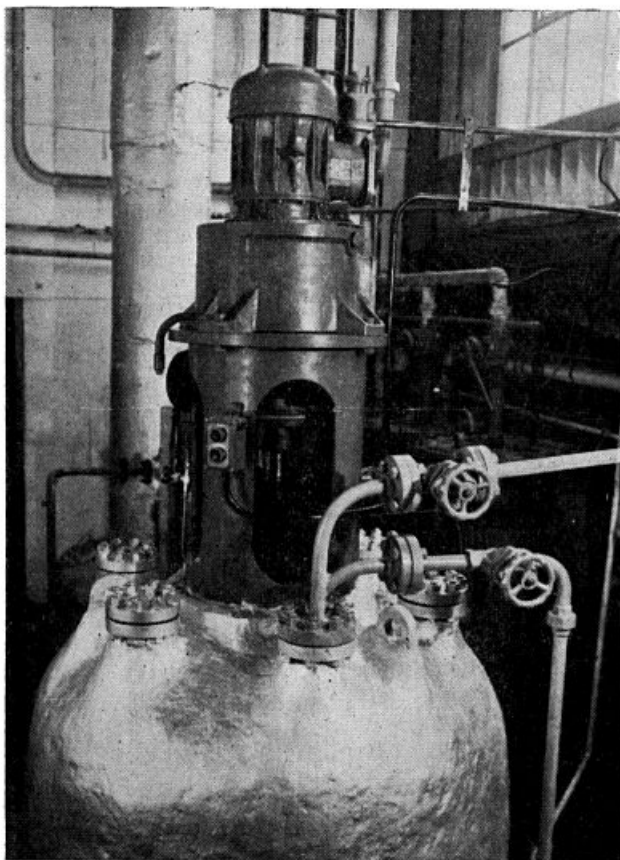


Fig. 4. The reactor for pyrrolidone production with a vacuum still in the background.

giving the product as a fine free-flowing powder. The polyvinylpyrrolidone recovered from the dryer has a water content normally in the region of 1.2—1.7 per cent. As the polymer is hygroscopic, it must be packed hot into heat-sealed polythene liners enclosed in stout outer kegs.

At each stage of the synthesis, the intermediates are carefully purified by vacuum distillation to avoid side reactions at subsequent stages, as these would make eventual purification much more difficult.

The illustrations in the text show various items of the plant at various stages in the synthesis.

3. GENERAL PROPERTIES

Polyvinylpyrrolidone is a rather unique polymer in that it is soluble in both water and a very wide range of organic solvents.

POLYVINYLPIRROLIDONE SOLUBILITY

ALCOHOLS	ESTERS
Methanol	Ethyl acetoacetate
Ethanol	Butyl tartrate
Isopropanol	
N butanol	HALOGEN COMPOUNDS
Sec butanol	Methylene chloride
Isobutanol	Ethylene dichloride
N amyl alcohol	Ethylene dibromide
Isoamyl alcohol	Ethylene chlorhydrin
N hexanol	Chloroform
Sec hexanol	
Cyclohexanol	ALDEHYDES AND KETONES
Diethyl ethanol	Acetone
Ethylene glycol	Methyl ethyl ketone
Glycerine	Acetyl acetone
Propylene glycol	Cyclohexanone
Diacetone	Glyoxal
Methyl isobutyl carbinol	Crotonaldehyde
	Benzaldehyde
ETHERS	
Cellosolve	NITROGEN COMPOUNDS
	α Pyrrolidone
ACIDS LACTONES	Vinyl pyrrolidone
Acetic anhydride	Pyridine
Glacial acetic acid	Morpholine
γ Butyrolactone	Nitrobenzene
Oleic acid	Acrylonitrile

Based on the preparation of 10 per cent solutions at room temperature.

Certain substances, for example acetone, can give rise to some difficulty as, although anhydrous polyvinylpyrrolidone will dissolve in anhydrous acetone, in the presence of only a little water the polymer tends to separate as a sticky second phase and for this reason such solvents are best avoided. Although polyvinylpyrrolidone itself is insoluble in hydrocarbons, solutions

EFFECT OF DILUENTS ON POLYVINYLPIRROLIDONE SOLUBILITY

Solvents	Ml. of Diluent added to Procure a Cloudy Mixture with 20 ml. of P.V.P. Solution				
	Benzene	Xylene	White Spirit	Ether AR	Ethyl Acetate
Chloroform (AR.) ..	23	11	7	16	—
I.M.S.	32	15	6	26	—
Cellosolve	>100	>100	20	46	200
Nitrobenzene ..	18	5	4	unsuitable	22
Methancl (Tech.) ..	>100	49	unsuitable	52	>100

Based on 10 per cent solution of P.V.P.

Fig. 12. Solubility of polyvinylpyrrolidone in organic solvents.

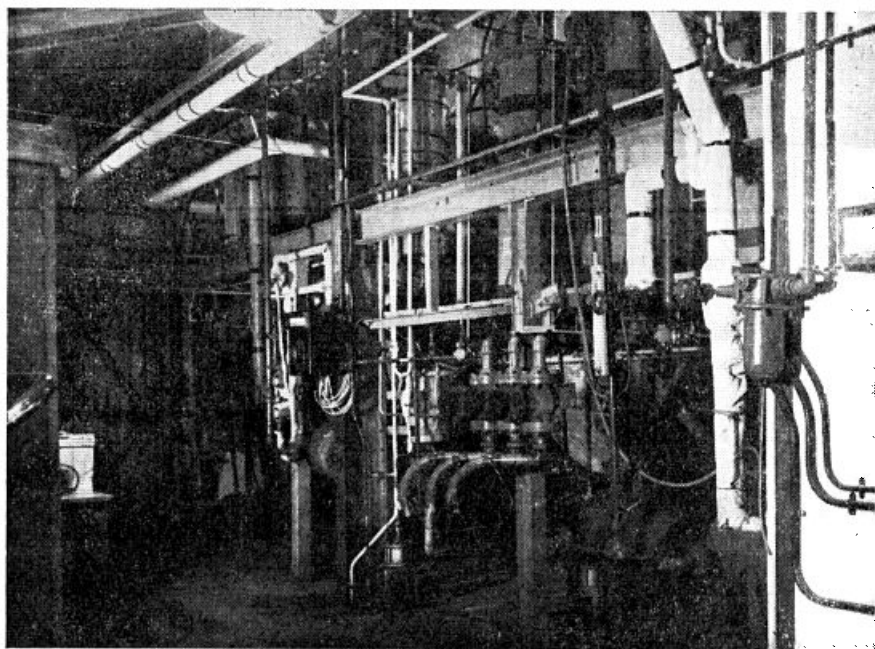


Fig. 5. General view of the purification section with a vacuum receiver shown in the foreground.

in powerful solvents will tolerate considerable dilution with hydrocarbons ; this is useful in certain applications.

Apart from its unique solubility properties, the polymer has the novel property of forming complexes with many substances very varied in chemical structure—for example, dyestuffs, iodine, antibiotics, insulin, etc.—and many industrial and pharmaceutical applications have been developed which take advantage of this property.

Apart from this, polyvinylpyrrolidone behaves in many ways in a manner typical of the natural proteins such as albumin, and is capable of tanning by prolonged heating or by treatment with tanning agents—for example, resorcinol, tannic acid, etc. It is also possible to form stable gels of the polymer by treatment with persulphates.⁵

In manufacturing the polymer it is possible, by the suitable adjustment and choice of catalysts, to prepare materials with K values ranging from about 20 to about 100, the corresponding mean molecular weights lying somewhere between 10,000 and 700,000. The K value of the polymer is, of course, a function defining the mean molecular weight of the material, and is determined by measuring the relative viscosity of an aqueous solution

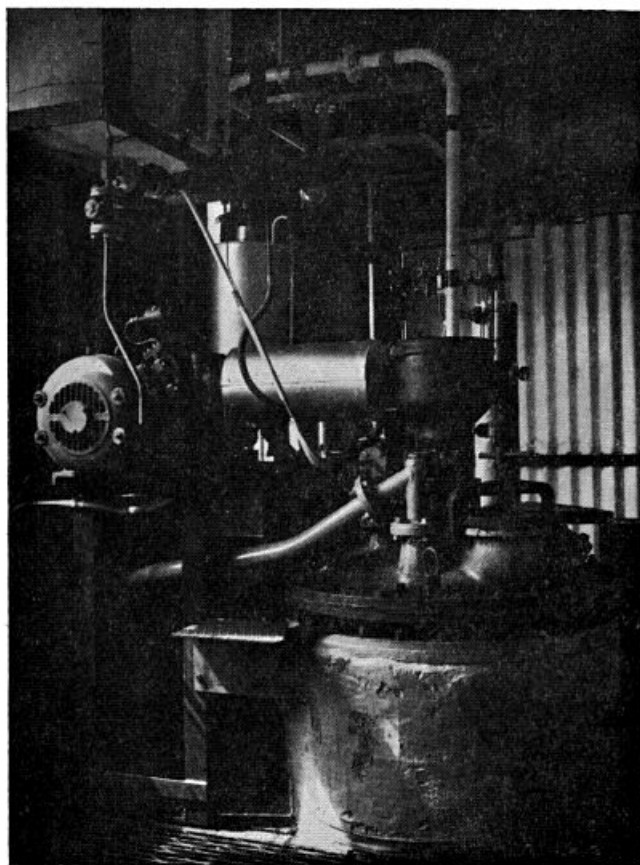


Fig. 6. A general view of the vinyl pyrrolidone polymerisation plant.

containing 1 per cent w/v of total solids using a suitable viscometer. The K value is then calculated in accordance with the following equation.

K value = 1000 k, where

$$\text{Log}^n \text{rel} = \frac{75k^2}{1 + 1.5k} + k$$

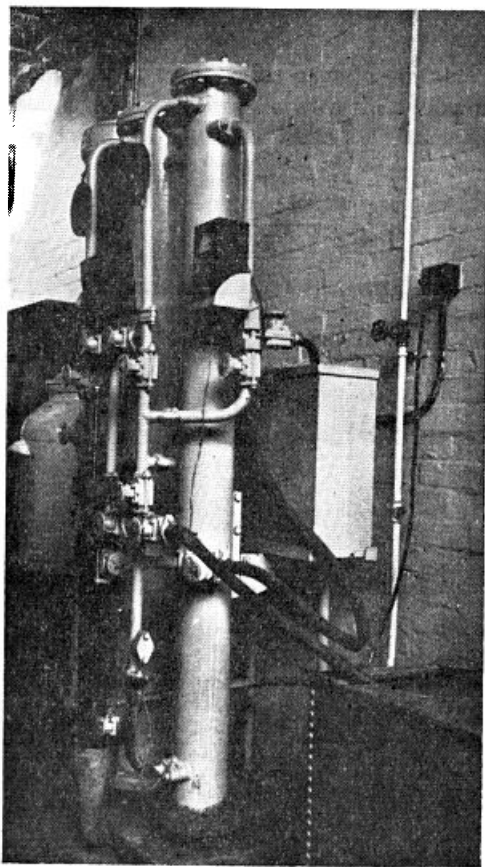


Fig. 7. The water de-ionisation unit used to provide water for carrying out the polymerisation of vinyl pyrrolidone monomer.

For most purposes a polymer having a K value between 30 and 35 appears to be most useful. The complex-forming ability of polyvinylpyrrolidone does not appear to be much affected by the molecular weight, and for film-forming uses, this medium molecular weight material gives solutions of reasonable viscosity. High molecular weight materials, as one



Fig. 8. The control room of the acetylene high-pressure building.

would expect, give solutions of extremely high viscosity, and these may find application as special-purpose thickening agents, etc., but they are otherwise of relatively little commercial interest in this country at the present time.

4. COSMETIC AND TOILET PREPARATION USES OF POLYVINYLPIRROLIDONE

(a) *General*

Apart from the general properties of polyvinylpyrrolidone reviewed above, the cosmetic chemist will be interested to know that it is a stable substance, uniform in its properties and, as far as we know, without harmful physiological effects, although clearly in any new application it is essential to check this by the usual methods.

The study of the possible uses of polyvinylpyrrolidone in cosmetics and toilet preparations appears to have originated from work carried out in America by Shelanski, Shelanski and Cantor,⁶ who demonstrated that polyvinylpyrrolidone is substantive to human skin and hair. The resultant films leave the skin smooth and soft to the touch, and when the polymer, suitably formulated, is applied to the hair it imparts a conditioning effect, enhancing its appearance and manageability.

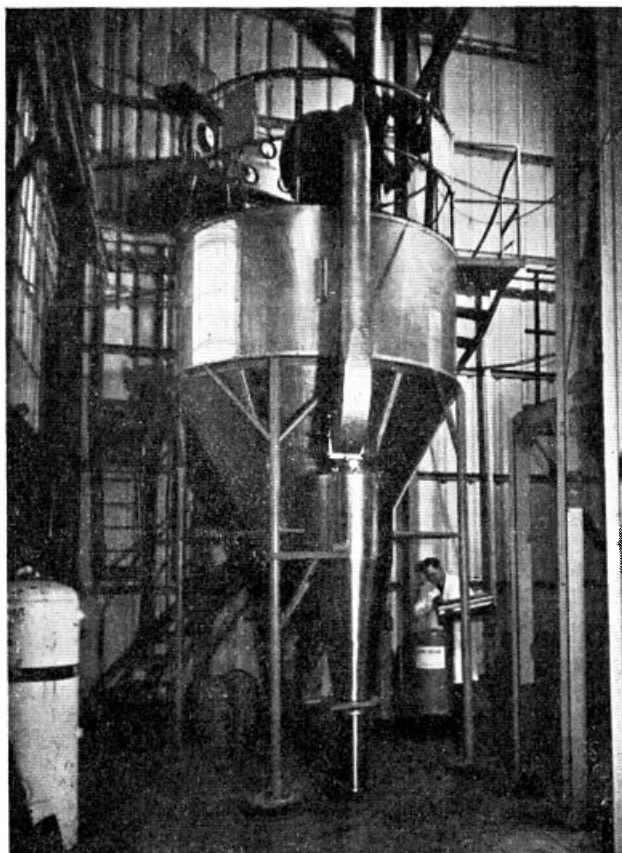


Fig. 9.

View of the spray dryer for the final recovery of solid polyvinylpyrrolidone.

The combination of these somewhat remarkable properties has encouraged cosmetic chemists to evaluate polyvinylpyrrolidone for a wide variety of uses employing these special characteristics. It is not suggested that polyvinylpyrrolidone be used simply as a water-soluble binder and thickening agent, although it is suitable for use in this way. The polymer is clearly too expensive to compete with the older materials, and it must be pointed out that the lengthy synthesis of the product rules out the possibility of it ever becoming very much cheaper.

Attention has therefore been primarily directed to developing those uses where the polymer's special properties can be used to advantage as a bonus over its more normal properties as a water-soluble film former and binder.

*(b) Hair Preparations**(i) Hair Lacquers and Wave Sets*

The first cosmetic products based on polyvinylpyrrolidone to reach large-scale commercial production in the U.S.A. and Europe have been hair lacquers, wave sets and other allied hair sprays.⁷ It has been stated⁸ that in the U.S.A. in 1955 somewhere between thirty-five and thirty-eight million aerosol cans of polyvinylpyrrolidone-based hair spray were sold, and at the time this information was published it was claimed that sales were still increasing rapidly. These sales, in fact, accounted for something in the region of 70 per cent of the total U.S. output of hair sprays in that year.

Hair lacquers have, of course, been known for many years, but the older type materials were usually based on shellac and other resins, and in the

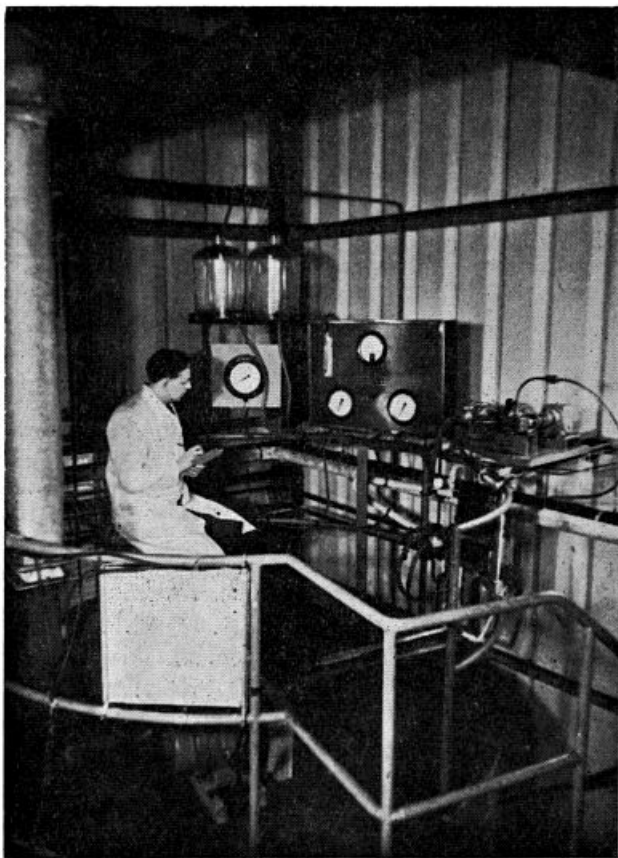


Fig. 10. Another view of the spray dryer for the final recovery of solid polyvinylpyrrolidone.

opinion of some users had marked defects. The advantage of polyvinylpyrrolidone-based hair sprays appears to lie in the fact that the polymer is soluble both in water and in organic solvents, and the lacquer, therefore, can be applied from a volatile solvent and yet be readily shampooed from the hair when required. When correctly compounded there is no tendency to dust or flake on the hair, and when packing in aerosol cans the compatibility of polyvinylpyrrolidone with the usual propellants overcomes problems of valve clogging. Polyvinylpyrrolidone hair sprays impart lustre to the hair, and probably owing to its hygroscopic nature improves hair manageability; this is said to be a marked improvement on the older type lacquers. The hair can be reset, moreover, for several days by using a damp hair brush and comb. It must be admitted that one does not obtain the crisp varnished appearance achieved with some of the older hair lacquers, but although some users think this a disadvantage, one gathers that many prefer the softer and more natural results obtained with polyvinylpyrrolidone.

Formulation is basically straightforward, but needs to be varied to meet different climatic conditions and different types of hair. A varied degree of crispness in the finish can also be provided to some extent to meet the needs of the user. All these are functions of the polyvinylpyrrolidone content and the type and quantity of plasticiser used. In a dry climate polyvinylpyrrolidone hair lacquers are said to be somewhat drying on the hair, and it seems to be a common practice⁹ in the U.S.A. to incorporate a humectant for this reason. In countries having a damp climate obviously a humectant is undesirable, and indeed in the U.K. a water-repellent plasticiser is used by most producers to make the hair finish reasonably damp-proof.

To deal with extreme conditions of moisture it has been suggested that the waterproofness of the hair spray can be increased still further by including modifying resins such as shellac, polyvinyl formal, etc., although the use of the former does not appear to find general favour.

In deciding the solids content of lacquers it is necessary to consider the type of hair.

Fine silky hair calls for lacquers containing as little as 2 per cent polyvinylpyrrolidone, but such a product would be quite useless on coarse wiry hair, where lacquers containing up to 7 per cent or 8 per cent of polyvinylpyrrolidone can be used. In commercial practice it seems usual to strike a compromise, and in the U.K. most lacquers appear to contain from about 4 to 6 per cent of polyvinylpyrrolidone.

The choice of plasticisers for polyvinylpyrrolidone is largely a matter of individual requirements. If water-repellency is to be achieved, either an oily plasticiser such as an alcohol-soluble lanolin derivative or isopropyl myristate can be used, or alternatively a phthalate plasticiser can be incorporated together with a small quantity of an alcohol-soluble silicone

Mixtures of plasticisers are also quite common, and are formulated to get special effects.

The crispness of the hair finish is largely a matter of plasticiser content. Using a polyvinylpyrrolidone content of 5 per cent one can use as little as $\frac{1}{2}$ per cent plasticiser without dusting or flaking and get a relatively crisp finish, but 1 per cent or 2 per cent of plasticiser results in softer and less visible finishes; the actual concentration depends to some extent upon the plasticiser used. High plasticiser contents have the advantage of giving increased lustre.

The usual solvent is ethyl alcohol, and when packing in aerosol cans this should be substantially anhydrous. For bulk sales and when packing in squeeze bottles many formulators prefer to incorporate a little water as this is said to improve hair manageability, but this is, of course, ruled out when using some plasticiser systems. Iso-propanol also appears to have received some consideration as a solvent, the attraction probably being the absence of duty, the lack of need for denaturants and its ready availability in anhydrous form for aerosol packing. In the past, I believe that its odour has given rise to some difficulty in perfuming, but it has recently been claimed that this need no longer be regarded as a serious difficulty.

Some of the commercial polyvinylpyrrolidone hair lacquers are marketed as combined lacquers/wave sets, but it seems more usual to formulate wave sets to provide a less permanent hair finish, their function being, of course, to set the hair into curls after shampooing. Such preparations are now often based on aqueous ethyl alcohol containing about 2% of polyvinylpyrrolidone together with plasticiser, perfume, etc. Some cosmetic chemists recommend the inclusion of a wetting agent, and indeed this is also done occasionally with hair lacquers intended for use in squeeze bottles which give a rather coarse spray, the idea presumably being to assist the lacquer to spread on the hair.

(ii) *Hair Creams*

Apart from hair lacquers and wave sets primarily intended for use by ladies, considerable interest is being shown, particularly in America, in the use of polyvinylpyrrolidone in men's hair fixatives.⁸ It is generally thought that the market here is larger in tonnage. Such preparations can either be similar in formulation to hair lacquers, and such preparations appropriately perfumed are said to be on the American market, or alternatively they can be made in the form of oily emulsions using polyvinylpyrrolidone in the aqueous phase. Such polyvinylpyrrolidone-stabilised creams are fine in texture and have a high surface gloss in the jar, at the same time imparting a surprising sheen to the hair without leaving it unduly oily. There appears to be no technical difficulty in the manufacture of such preparations.

(iii) Shampoos

The incorporation of polyvinylpyrrolidone into shampoos has been suggested,¹⁰ the advantages claimed being improved foam stability and an enhanced lustre on the hair owing to a residual film of polyvinylpyrrolidone after rinsing. American workers have also claimed that the incorporation of polyvinylpyrrolidone can reduce eye irritation, particularly in shampoos containing antiseptics.

(iv) Hair Dyes and Bleaches

The final suggested applications of polyvinylpyrrolidone in hair preparations are surprisingly near the established uses in the textile industry. It has been mentioned earlier that polyvinylpyrrolidone forms complexes with many dyestuffs, and it has been shown that when dyeing hair, carrying out this operation in the presence of polyvinylpyrrolidone can result in the polymer being deposited on the hair preferentially, the polymer film then taking up the dyestuff. The Shelanskis⁶ have suggested this phenomenon can be used to provide either more permanent tints on the hair or alternatively temporary colourings which can easily be washed out on shampooing. This appears paradoxical, but apparently is based on different polyvinylpyrrolidone concentrations and different modes of application. Almost certainly different types of dyestuffs are involved, but no experimental details have been published.

An interesting variant of this has recently appeared on the market, both in the U.K. and in the U.S.A.,¹¹ in the form of coloured polyvinylpyrrolidone hair lacquers. These have the virtue of providing stable temporary tints which can be applied to the hair at the same time as the lacquer and can be readily removed with the lacquer by shampooing. Presumably the advantage is that the hair is never actually dyed, and so cannot become damaged.

The use of polyvinylpyrrolidone with hydrogen peroxide for hair bleaching has also been suggested in America, where it has been claimed⁹ that the polyvinylpyrrolidone stabilises the hydrogen peroxide solution to give a more effective bleaching agent operating in the absence of either ammonia or ammonium salts.

(c) Pre-shave and After-shave Lotions

Polyvinylpyrrolidone is also being used in both pre-shave and after-shave lotions, particularly those for aerosol application, although this expensive method of packing hardly seems essential. Typical after-shave lotions are based on about $\frac{1}{2}$ per cent polyvinylpyrrolidone in 85 per cent ethyl alcohol, together with perfume. Such products can obviously be packed in glass aerosol containers if desired.¹² The polyvinylpyrrolidone is

said to reduce somewhat the sting of the spirit and to leave a smooth, slight film on the skin. In pre-shave lotions for use with electric razors the inclusion of polyvinylpyrrolidone should assist in conditioning the hair for shaving and again would leave a smooth film on the skin.⁸

(d) *General Make-up*

So far we have discussed applications of polyvinylpyrrolidone which result in the deposition of a transparent film. Apart from its excellent film-forming properties polyvinylpyrrolidone is also an excellent pigment binder and dispersing agent, and it is therefore not surprising that it has found application in the formulation of liquid make-up, pancake, compressed powder make-up and mascara. Such applications so far appear to have particularly aroused interest in Germany, and it has been claimed that such make-up leaves the skin smooth to the touch. In mascara I understand that the use of polyvinylpyrrolidone can result in a non-eye irritant preparation, but I believe that this can now be achieved by other means as well. It has been mentioned earlier, when discussing hair creams, that polyvinylpyrrolidone is an excellent emulsion stabiliser, and can therefore be used in the formulation of toilet emulsions, including pigmented emulsions such as tinted foundation creams. The use of polyvinylpyrrolidone in hormone cosmetic creams has been patented¹⁹ and the polymer may also find possible applications in the formulation of special purpose barrier creams.^{13,14}

In America they appear to be showing interest in the use of polyvinylpyrrolidone in lipsticks and in nail polish removers. The former application is possibly associated with polyvinylpyrrolidone's ability to form dyestuff complexes; the latter use is not fully understood.

(e) *Shaving Creams*

The use of polyvinylpyrrolidone in shaving creams has also been suggested,¹⁵ particularly for use in aerosol packs. One would expect that such shaving creams would leave the skin feeling particularly smooth, and in addition, as mentioned earlier under shampoos, the polymer is an excellent foam booster and stabiliser.

(f) *Tooth Pastes*

On the fringe of the toilet preparation class of product I would mention that the use of polyvinylpyrrolidone in tooth pastes has been patented.^{16,17,18} It is claimed that the polymer's complexing ability assists in the removal of tartar and in removing tobacco stains. It has also been suggested that polyvinylpyrrolidone can be used with advantage in the formulation of chlorophyll-containing tooth-paste.

(g) *Perfuming*

Perfume plays an important part in all cosmetic preparations, and attention must be drawn to the fact that polyvinylpyrrolidone is a reactive polymer and can form complexes with appropriate substances. In certain cases this can result in the precipitation or gelling of polyvinylpyrrolidone and certainly will result in a change in its viscosity. It is, of course, also possible that the odour of the perfume might change through such complexing. It is therefore essential to ensure that perfumes used with polyvinylpyrrolidone are fully compatible. Very little has been published on this subject, but we are informed that most perfume and perfume raw material suppliers are now aware of this problem and can advise on the choice of suitable compounds. This property of forming complexes with perfumes has resulted in suggestions that the polymer may be of interest as a possible perfume fixative, and we have been advised that such properties and possible applications are being actively studied both in this country and overseas.

Acknowledgement is made to the Directors of British Oxygen Research and Development Limited for permission to publish this paper, and to the various members of your industry for advice on the uses of polyvinylpyrrolidone in cosmetics.

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