Polymers Suitable for Increasing the Viscosity of Formic Acid: Application to the Printing of Wool with Reactive Dyes

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Synopsis

A study has been made of the properties of formic acid solutions of several polymers in relation to their usefulness as thickening agents for printing pastes composed of reactive dyes dissolved in formic acid.   Polybases effectively increase the viscosity of formic acid to a satisfactory level but because of their ionization in formic acid, they inhibit the uptake of dye on wool due to the "salt effect" previously described.   Incorporation of styrene with the base into a copolymer dilutes the salt effect but not sufficiently to be of practical importance.   It was found that high molecular weight poly(ethylene glycol) and several natural carbohydrate gums effectively increased the viscosity without affecting the dye uptake.   Moreover, contrary to their behavior in aqueous solutions, these natural gums did not react with the reactive dyes in formic acid solution.   It is suggested that these dyes do not react with wool itself in formic acid solution, but reaction takes place only after the formic acid has been removed by washing.

INTRODUCTION

It has recently been demonstrated[1-3] that wool may be dyed at room temperature within 1–2 min.   This is achieved by using concentrated (>85%) formic acid instead of water as the solvent medium in the dyebath.   The influence of formic acid has been attributed[1,2] to two main factors: (a) the ability of formic acid to swell wool,[4] thereby lowering the barriers to diffusion of dye within the fiber; the swelling is probably a result of the large electrostatic repulsions set up by the high net charge on the wool keratin in formic acid; and (b) the favorable conditions for electrostatic attraction between the dye molecule and the wool protein.   The carboxyl groups on the keratin are largely unionized in formic acid, so that the protein attains its maximum net positive charge which is possibly augmented by protonation of the amide groups of the protein.[5-7]   On the other hand, the sulfonic acid groups of the dye molecule with their considerably lower pK_a values remain ionized and are attracted to the wool protein.

A particularly useful class of dyes for which this method of dyeing is

effective is that including the so-called "reactive" dyes.   In addition to the usual SO_3^- groups, these contain active groups (usually halogen) which react with the wool protein so that the dye is covalently bound to the wool. As might be expected, this results in high washfastness properties for this group of dyes.

By the addition of suitable "thickening agents" to increase the viscosity of the dye solution in formic acid, screen printing of wool fabrics may be carried out and is used commercially in Australia.   With nonreactive dyes a wide variety of natural and synthetic polymers is available for aqueous printing pastes, and most of these are suitable for thickening formic acid. When using reactive dyes the range of thickeners available for use in aqueous pastes is considerably reduced.[8]   Dye manufacturers recommend the avoidance of thickeners containing groups such as hydroxyl, since these thickeners compete with wool for reaction with the dye and form reaction products which are nonsubstantive to wool and which may mark off during further processing.   Alginate thickeners are normally recommended for printing pastes involving reactive dyes but these are insoluble in formic acid and are therefore inapplicable to this system.   We have therefore attempted to find suitable polymers which give solutions of high viscosity in formic acid but which do not contain groups capable of reacting with the reactive dyes.   This paper reports some properties of formic acid solutions of several polymeric thickening agents and their influence on the dyeing of wool with reactive dyes.

EXPERIMENTAL AND RESULTS

Polymer Preparation

The polymers were prepared by heating under reflux for 12 hr. the monomer, or monomer mixture, with an equal weight of dried, distilled methyl ethyl ketone.   Molecular weight was varied by changes in the initiator concentration, the levels used being 2, 1, and 0.5% on weight of monomer. Azobisisobutyronitrile was used as the initiator to minimize chain branching and to avoid the amine catalyst decomposition sometimes encountered with peroxide.[9]

Since no allowance was made for the reactivity ratios of the monomer, the copolymers would not be expected to be "distributed."

With the exception of the poly-4-vinylpyridine and 4-vinylpyridine–styrene (75:25) copolymer series which were insoluble in methyl ethyl ketone, all polymers gave colorless to brown solutions.

The poly(ethylene glycols) used were PEG 400, 1000, and 6000 supplied by the Shell Chemical Co. (Aust.), Pty. Ltd., and Carbowax 20M (molecular weight 20,000) marketed by Union Carbide Australia Ltd.

Isolation

The polymers were isolated as follows (the figures given are based on 10 g. of monomer).

2-Vinylpyridine Polymers and Copolymers. The method previously described by Strauss and Jackson[10] was used. The polymers were dried in a rotary evaporator at 40°C. and dissolved in toluene (60 ml. analytical reagent) and pyridine (6 ml. analytical reagent) and the resultant solution added dropwise to light petroleum (700 ml., b.p. 90–120°C.). The precipitated polymer was washed by decantation with petroleum ether and vacuum-dried at 40°C.

Vinylpyrrolidone Polymers and Copolymers. The homopolymers were dried in a rotary evaporator at 40°C. and the solid redissolved in water and freeze-dried.

The copolymers were diluted with methyl ethyl ketone (100 ml.) and these solutions added dropwise to water (1 liter). The precipitated copolymers were dried at 40°C. under vacuum.

4-Vinylpyridine Polymers and Copolymers. The methyl ethyl ketone was removed in a rotary evaporator at 40°C. The residue was dissolved in pyridine (50 ml.) and precipitated by adding dropwise to toluene (700 ml.). The polymers separated as large lumps which were air-dried, finely ground and vacuum-dried at 40°C. to remove pyridine.

tert-**Butylaminoethyl Methacrylate Polymers and Copolymers.** The polymer solutions were diluted with methyl ethyl ketone (60 ml.) and dropped into water (1500 ml.) with rapid stirring. The sticky precipitate which formed was air-dried, finely ground, and vacuum-dried at 40°C.

Characterization of Polymers

Viscosity measurements in nonionizing solvents were carried out in an Ostwald viscometer with a flow time for the solvent of at least 100 sec. All solutions were filtered through sintered glass disks (porosity 4) before measurements were made.

TABLE I

Reduced Viscosities η_{red} in Methyl Ethyl Ketone ($C = 0.5\%$) and Formic Acid ($C = 5\%$) and Dye Uptake for Poly-2-vinylpyridine and its Copolymers with Styrene

Sample	Initiator Monomer %	η_{red} (methyl ethyl ketone)	η_{red} (formic acid)	Dye uptake
Poly-2-vinylpyridine	2	0.091	0.76	1
"	1	0.112	1.23	1
"	0.5	0.141	2.03	1
2-Vinylpyridine–styrene (75:25) copolymer	2	0.089	0.63	2
"	1	0.108	0.91	2
"	0.5	0.150	1.78	2
2-Vinylpyridine–styrene (50:50) copolymer	2	0.101	0.63	3
"	1	0.120	0.75	3
"	0.5	0.143	1.20	3

TABLE II

Reduced Viscosities η_{red} in Ethanol ($C = 0.5\%$) or Methyl Ethyl Ketone
($C = 0.5\%$) and Formic Acid ($C = 5\%$) and Dye Uptake for Poly-4-vinylpyridine
and its Copolymers with Styrene

Sample	Initiator Monomer %	η_{red} (eth- anol)	η_{red} (methyl ethyl ketone)	η_{red} (formic acid)	Dye up- take
Poly-4-vinylpyridine	2	0.24	—	1.24	2
"	1	0.38	—	2.68	2
"	0.5	0.48	—	4.09	2
4-Vinylpyridine–styrene (75:25) copolymer	2	0.16	—	0.74	4
4-Vinylpyridine–styrene (75:25) copolymer	1	0.25	—	1.47	4
4-Vinylpyridine–styrene (75:25) copolymer	0.5	0.31	—	2.07	4
4-Vinylpyridine–styrene (50:50) copolymer	2	—	0.099	0.53	6
4-Vinylpyridine–styrene (50:50) copolymer	1	—	0.128	1.03	6
4-Vinylpyridine–styrene (50:50) copolymer	0.5	—	0.168	1.82	6

TABLE III

Reduced Viscosities η_{red} in Methyl Ethyl Ketone ($C = 0.5\%$) and Formic Acid
($C = 5\%$) and Dye Uptake for Poly(tert-butylaminoethyl Methacrylate) and its
Copolymers with Styrene

Sample	Initiator Monomer %	η_{red} (methyl ethyl ketone)	η_{red} (formic acid)	Dye uptake
Poly(tert-butylaminoethyl meth- acrylate)	2	0.112	0.51	3
Poly(tert-butylaminoethyl meth- acrylate	1	0.114	0.88	3
Poly(tert-butylaminoethyl meth- acrylate)	0.5	0.140	0.97	3
tert-Butylaminoethyl methacrylate– styrene (75:25) copolymer	2	0.080	0.31	5
tert-Butylaminoethyl methacrylate– styrene (75:25) copolymer	1	0.110	0.53	5
tert-Butylaminoethyl methacrylate– styrene (75:25) copolymer	0.5	0.162	0.65	5
tert-Butylaminoethyl methacrylate– styrene (50:50) copolymer	2	0.074	0.27	8
tert-Butylaminoethyl methacrylate– styrene (50:50) copolymer	1	0.129	0.43	8
tert-Butylaminoethyl methacrylate– styrene (50:50) copolymer	0.5	0.176	0.87	8

The poly-4-vinylpyridine and 4-vinylpyridine–styrene (75:25) copolymer series were measured in ethyl alcohol and the polyvinylpyrrolidone in methyl alcohol. The remaining polymers were characterized in methyl ethyl ketone. The results are shown in Tables I–IV as reduced viscosities, $\eta_{red} = [(\eta/\eta_0) - 1]/C$, where η/η_0 is the relative viscosity and C is the concentration (0.5%).

Viscosities of the polymers were also measured in formic acid. A uniform concentration of 5% (w/v) polymer in the solvent was used, this concentration being set arbitrarily as the upper limit which might be used in practical application. In the majority of cases the viscosity of the solution was several times that of the solvent and in order to avoid excessively long times of flow for the solution, a viscometer with a time of flow for the solvent of only 30 sec. was used. However, this time of flow was reproducible to ±0.1 sec. The reduced viscosities of these solutions are in Tables I–IV.

TABLE IV
Reduced Viscosities η_{red} in Methanol ($C = 0.5\%$) and Formic Acid ($C = 5\%$) and Dye Uptake for Polyvinylpyrrolidone

Sample	Initiator Monomer %	η_{red} (methanol)	η_{red} (formic acid)	Dye uptake
Polyvinylpyrrolidone	2	0.123	0.21	10
"	1	0.139	0.23	10
"	0.5	0.119	0.18	10

Dye Uptake

The influence of the polymers on the uptake of a reactive dye from solutions was measured in the following manner: 30 mg. of the dye Procion Brilliant Orange, 2RS (I.C.I. Ltd., England), was dissolved in 10 ml. of a formic acid solution of polymer. Routinely the polymer concentration was 5% (w/v). A 300-mg. portion of wool top (Australian Merino 64's) was immersed in this, and after the appropriate time (2 min. unless otherwise

TABLE V
Effect of Polymer Concentration and Time of Immersion of Wool on Dye Uptake for Poly-4-vinylpyridine–Styrene (75:25) Copolymer

Concentration of polymer, %	Time, min.	Dye uptake
5	1	4
2	1	3
2	5	5
2	20	6
2	60	8

stated) the wool was removed from the dye solution, washed well with running water, and dried. The dyed sample was then compared with a wool sample which had been dyed under identical conditions, except for the omission of polymer, and the dye uptake measured subjectively by grading the color intensity on a scale 1–10, where 10 represents the intensity of wool dyed in the absence of polymer. The results are shown in Tables I–IV and Table VI. Experiments were also done (using the highest molecular weight copolymer of 4-vinylpyridine with 25% styrene) in which the concentration of polymer was varied and also the time of immersion of the wool in the dye solution. These results are shown in Table V.

TABLE VI
Reduced Viscosities η_{red} in Formic Acid (C = 5%) and Dye Uptake for
Poly(ethylene Glycols) of Different Molecular Weights

Molecular weight	η_{red} (formic acid)	Dye uptake
400	0.03	10
1,000	0.13	10
6,000	0.32	10
20,000	1.24	10

DISCUSSION

As polymers which might fulfill one or another of the requirements of thickening formic acid and of inertness to reactive dyes we synthesized several series of polybases of differing molecular weight from the monomers 2-vinylpyridine, 4-vinylpyridine, and *tert*-butylaminoethyl methacrylate (Tables I–III) at three different molecular weight levels. The reduced viscosity of each polymer in formic acid was considerably greater than the corresponding viscosity in the nonionizing solvents fulfilling the first of the required conditions. The increase in viscosity in formic acid is probably due to the ionization of the basic groups of the polymer in formic acid (which has a relatively high dielectric constant), and the resultant conversion of the polymer to a more rodlike conformation of higher axial ratio. Conversion to a more rodlike structure is also indicated if we consider the ratios of η_{red} for the highest and lowest molecular weight polymers in each series. For each polymer this ratio is greater in formic acid than in the nonionizing solvent, and it has been shown that the variation of viscosity with molecular weight is greater for rodlike than for random-coil conformations.[11] (Although this behavior applies strictly to intrinsic viscosities, it would be expected that the slopes of the η_{red} versus C curves would be approximately constant for any one polymer within a molecular weight series, and hence the same general relations between viscosity and molecular weight should hold for viscosities unextrapolated to zero concentration.) The increase in viscosity in transferring to formic acid solutions is somewhat less for the *tert*-butylaminoethyl methacrylate polymers than for the vinyl-

pyridine polymers. This is not due to differences in the degree of ionization, since the value[12] of pK_a for the secondary amine polymer (7.5) is considerably greater than that[13] for poly-4-vinylpyridine) (3.0), but probably results from the more limited tendency of the methacrylate polymer to extend as compared with the vinylpyridine polymers for the same degree of polymerization.

The values of η_{red} in nonionizing solvents are higher for the 4-vinylpyridine series than for the other two polymers, even though the initiator concentrations were the same in all cases. These apparently higher molecular weights are probably a result of the precipitation of poly-4-vinylpyridine from the solvent medium (methyl ethyl ketone) during polymerization: it is well known[14] that polymerization in heterophase systems decreases the possibility of termination reactions thereby leading to higher degrees of polymerization.

In contrast to the above polymers, the increase in viscosity of formic acid solutions of the polyvinylpyrrolidone series over methanol solutions is relatively small and could be explained simply by the difference in solute concentration in the two solvents (5 and 0.5%, respectively) rather than by any conformational changes. These polymers are very much weaker bases than the other three, and it is not to be expected that appreciable ionization and extension of the molecule will occur in formic acid.

There are also marked differences between polyvinylpyrrolidone and the remaining three polybases in their influence on the uptake of dye by wool from formic acid solutions. Polyvinylpyrrolidone has very little effect on the dye uptake, whereas the other polymers strongly inhibit it. It has been shown previously[1] that even low concentrations of inorganic salts (e.g., NaCl, KCl) inhibit the uptake of dye from formic acid, and it is probable that ionization of the polybases has a similar effect. Polyvinylpyrrolidone, being a much weaker base, has no influence. Although all three ionizable polymers exhibit this "salt effect," they show small differences among themselves in their influence on dye uptake which seem to be related to their extensibility in formic acid. Thus, poly(*tert*-butylaminoethyl methacrylate), which showed the smallest viscosity increase in formic acid when compared to methyl ethyl ketone, also inhibited dye uptake least of the three polybases.

Within each series, molecular weight appears to have little influence on dye uptake when compared at the same weight concentration. Moreover it can be seen from the limited data in Table V that changes in polymer concentration also have little effect on the dye uptake. It therefore did not seem necessary to compare the effects of the polymers at the same viscosity as well as at the same concentration. The uptake of dye can be increased by lengthening the time of contact of the wool with the dye solutions containing ionizable polymers. However, for acceptable results the times of contact are so long as to be unattractive commercially.

An attempt was made to improve the dye uptake from solutions of the ionizable polymers by synthesizing polymers in which styrene was incor-

porated at two different levels (25 and 50% w/w) with each of the mono-
mers already described.   It was predicted that the styrene would have two
main effects (*1*) as an unionizable residue of low dielectric constant it should
dilute out the "salt effect" of the polymer; (*2*) since polystyrene is insolu-
ble in formic acid, the incorporation of styrene into the polybase should be
equivalent to adding a nonsolvent to the system and lead to an increase in
the viscosity of the polymer–formic acid system.   The reduced viscosities in
methyl ethyl ketone of the poly-2-vinylpyridine and poly(*tert*-butyl-
aminoethyl methacrylate) copolymers (Tables II and III) indicate that
they are comparable in molecular weight with the homopolymers.   The
50:50 copolymers of poly-4-vinylpyridine (Table I) were soluble in the
polymerization solvent and followed normal solution kinetics, so that the
copolymers fell into the same molecular weight range as the copolymers in
Tables II and III.   The copolymers of 4-vinylpyridine containing 25%
styrene were only partially soluble during polymerization and gave a
molecular weight range intermediate between those of the homopolymers
and the 50:50 copolymers.   Copolymers of vinylpyrrolidone and styrene
were insoluble in formic acid at both levels of incorporation and were not
further studied.   Other copolymers of vinylpyrrolidone and styrene were
not evaluated because of the difficulty in getting even an approximately
distributed polymer due to the tendency to form polystyrene at the expense
of the copolymer.[15]

The reduced viscosities of the copolymers in formic acid are in each case
lower than that of the corresponding homopolymer and decreases with
increasing styrene content.   This implies that the nonsolvent effect of the
styrene is more than counterbalanced by the dilution of the ionized groups
on the molecule, so that the copolymers are not as extended in formic acid
as the homopolymers.   This reduction in the ionogenic nature of the
copolymers is also reflected in their dyeing properties, since incorporation
of styrene leads in all cases to an increase in the dye uptake by the wool
although not sufficient to be of practical value.

The contrast between dye uptake in the presence of the ionizable poly-
mers with that in the presence of polyvinylpyrrolidone suggested the
evaluation of other macromolecules with groups capable of strong solute–
solvent interaction but which would not ionize in formic acid solutions.
A range of commercially available poly(ethylene glycol) polymers of differ-
ing molecular weight was examined, and Table VI shows that the highest
molecular weight samples produced a considerable increase in viscosity
without inhibiting the dye uptake.   Since these polymers have hydroxyl
groups at either end of the polymer chain, it was possible (by analogy with
aqueous systems) that these would react with the dye leading to the deposi-
tion of appreciable quantities of a nonchemically bound reaction product on
the wool.   However, extraction for 45 min. at 95°C. with 80% (v/v) pyri-
dine produced no more color in solution for the wool dyed in the presence of
the lowest molecular weight poly(ethylene glycol) than for a control sample
dyed in the absence of thickener.   This was also true for an extreme case

where wool was dyed in the presence of ethylene glycol itself. It therefore appears that, in contrast to aqueous solution, the reactive dyes do not react with hydroxyl groups in the presence of formic acid.

Similarly, very little color could be extracted by 80% pyridine from wool dyed in the presence of *tert*-butylaminoethyl methacrylate polymers, even allowing for the lower dye uptake in the presence of these polymers. This series of polymers was originally included only to provide models of a higher degree of basicity than the vinylpyridine polymers, since it was expected that the secondary amine group would react with the dye. However the extraction results indicate that, as with the hydroxyl groups, this does not occur in formic acid. Extending these ideas to wool itself, it seems probable that, although the reactive dye penetrates the fiber rapidly in formic acid it may do so as an acid dye, chemical reaction occurring after removal of the formic acid by washing. Only then is the HCl reaction product liberated and removed by further washing:

$$\text{Wool—H} + \text{Cl—Dye} \rightleftharpoons \text{Wool—Dye} + \text{HCl}$$
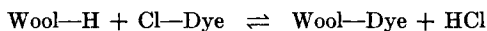
Therefore in the thickening of formic acid solutions of dyes it is more necessary to avoid reagents which can undergo salt formation with the formic acid than to avoid those with potentially active hydrogen atoms. This led us to examine thickening agents which we had found satisfactory for use with nonreactive dyes. These were mainly natural gums, e.g., Meypro Gum, Sandoz (Australia) Ltd.; Karachi Gum, Monsanto (Australia); contrary to previous indications, these had no adverse effect on the printing of reactive dyes from formic acid solution and are probably the most satisfactory for commercial use.

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Résumé

On a étudié les propriétés des solutions dans l'acide formique de plusieurs polymères en relation avec leur utilité comme agent épaississant pour des pâtes à imprimer, composées des colorants réactifs dissous dans l'acide formique. Des polybases augmentent, en effet, la viscosité de l'acide formique d'une façon satisfaisante, mais à cause de leur ionisation dans l'acide formique, ils inhibent la fixation du colorant sur la laine provoquée par l'effet de sel décrit antérieurement. L'incorporation de styrène avec la base, sous forme d'un copolymère, diminue l'effet de sel mais pas suffisamment pour avoir une importance pratique. On a trouvé que le poly-éthylène glycol de haut poids moléculaire et plusieurs gommes naturelles d'hydrate de carbone augmentent effectivement la viscosité sans influencer la fixation du colorant. En outre, contrairement à leur comportement dans des solutions aqueuses, ces gommes naturelles ne réagissent pas avec les colorants réactifs dans la solution d'acide formique. On a suggéré que ces colorants ne réagissent pas avec la laine elle-même dans la solution d'acide formique, mais que la réaction se produit uniquement après avoir éliminé l'acide formique par lavage.

Zusammenfassung

Eine Untersuchung der Eigenschaften der Lösungen einiger Polymerer in Ameisensäure in bezug auf ihre Verwendbarkeit als Verdickungsmittel für Druckpasten aus Reaktivfarbstoffen in Ameisensäure wurde durchgeführt. Polybasen erhöhen die Viskosität der Ameisensäure auf eine befriedigende Höhe, infolge ihrer Ionisierung in Ameisensäure verhindern sie aber wegen des schon früher beschriebenen "Salz-Effektes" die Aufnahme des Farbstoffes durch die Wolle. Einführung von Styrol mit der Base in ein Copolymeres verdünnt zwar den Salzeffekt, jedoch nicht in genügendem Ausmass, um praktische Bedeutung zu besitzen. Es wurde gefunden, dass hochmolekulares Polyäthylenglycol sowie einige natürliche Kohlenhydratgummi die Viskosität wirksam erhöhen, ohne die Farbstoffaufnahme zu beeinflussen. Ausserdem reagierten diese Naturgummi im Gegensatz zu ihrem Verhalten in wässriger Lösung in Ameisensäurelösung nicht mit den Reaktivfarbstoffen. Es wird angenommen, dass diese Farbstoffe mit Wolle nicht in Ameisensäure reagieren, sondern dass die Reaktion erst nach Entfernung der Ameisensäure durch Waschen stattfindet.