

STABLE TANNIN BASED POLYMER

This invention relates to a process for the manufacture of a tannin based polymer flocculant which does not gel and which remains stable over a period of several months.

5 British Patent No. 899,721 discloses a process for flocculation of suspensions such as sewage industrial waste and natural water in which a flocculating agent is applied comprising the reaction product between a tannin, formaldehyde and an amino or ammonium compound. The
10 advantage of using such a flocculating agent is said to be that it does not affect the pH of the suspension solution nor the dissolved inorganic solids content of the final water. No details are given on how to make this flocculating agent and merely reacting the three ingredients produces a
15 reaction product which tends to form a gel; it does not remain in the liquid form for substantial periods of time.

It is an object of this invention to produce a tannin based polymer flocculant which will not gel or solidify over a period of several months while continuing
20 to provide commercially acceptable performance for use in water purification and demulsification.

According to the present invention an aqueous solution of a tannin based polymer compound which is suitable for use as a flocculant is made under controlled reaction
25 conditions. We have discovered that the key to obtaining a successful commercial product which has a good shelf life, typically at least 3 months under ambient conditions, is the ability to monitor the reaction and stop it when the viscosity reaches a critical intermediate range.

30 Accordingly the present invention provides a method of forming an aqueous solution of a tannin based polymer which comprises heating an aqueous mixture of a tannin, an amino compound which contains, or is capable of generating under the reaction conditions, a primary amino

group, and an aldehyde or a compound which generates an aldehyde group under the reaction conditions, under acidic conditions, the molar ratio of the primary amino groups of the amino compound to the tannin repeating unit being 1.5:1 to 3.0:1, at 150°-200°F (66°-93°C) until the reaction product which forms has a viscosity which is within the key intermediate viscosity range for the reaction system, said range being that for the said system which permits the resulting product to have a desired shelf-life, said viscosity range preferably being 2-100 cps when measured at 180°F (82°C) on a Brookfield LVT viscometer, and (c) terminating the reaction when the viscosity has reached the condition specified above and, if necessary, adjusting the solids content of the liquid to 20 to 60% by weight and the pH to a value of less than 3.0. Thus the reaction mixture is heated until a reaction product forms which has an intermediate viscosity within the desired range which is referred to as the system key intermediate viscosity range. This system key intermediate viscosity range is determined for each reactant system to be used. It is a narrow intermediate viscosity range that is experimentally determined which permits the resulting product to have a long shelf life. These narrow system key intermediate viscosity ranges are generally within the range of from 2-100 cps when measured at 180°F (82°C) on a Brookfield LVT viscometer. The reaction is terminated when the system key intermediate viscosity has been reached.

In preferred embodiment using tannin in the form of a spray-dried quebracho powder, formaldehyde and monoethanol amine, the system key intermediate viscosity range is from about 38-40 cps when measured at 180°F (82°C) on a Brookfield LVT viscometer. The reaction liquid is cooled and adjusted to have solids content from about 40 to 45% by weight and a pH preferably in the range of 2.3 to 2.6. This aqueous solution remains stable and does not gel for up to six months; it can be used as a flocculant for treating wastewater.

The tannin component can be obtained from the various wood and vegetation materials found throughout the world. Tannins are a large group of water-soluble, complex organic compounds. Almost every tree or shrub that grows contains some tannins in the leaves, twigs, barks, wood or fruit. Examples of barks are wattle, mangrove, oak, eucalyptus, hemlock, pine, larch and willow. Examples of woods are the quebracho, chestnut, oak and urunday. Examples of fruits are myrobalans, valonia, divi-divi, tara, and algarroBILLA. Examples of leaves are sumac and gambier and examples of roots are canaigre and palmetto. Among the preferred materials is the quebracho wood. A spray-dried quebracho powder is sold by Canada Packers, Ltd. as Mimosa Extract.

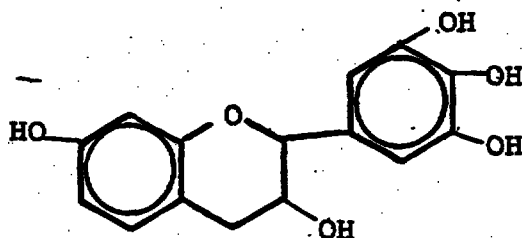
These natural tannins can be categorized into the traditional "hydrolyzable" tannins and "condensed tannins" as disclosed by A. Pizzi in "Condensed Tannins for Adhesives", Ind. Eng. Chem. Prod. Res. Dev. 1982, 21, 359-369. condensed tannin extracts are those manufactured from the bark of the black wattle tree (or mimosa tannin of commerce), from the wood of the quebracho tree (Spanish: Quebra hacha, axe-breaker,) from the bark of the hemlock tree, and from the bark of several commonly used pine species. The preparation of wattle and quebracho extracts is a well established industrial practice and such extracts are freely available in considerable amounts.

Condensed tannin extracts, such as wattle and quebracho, are composed of approximately 70% polyphenolic tannins, 20% to 25% nontannins, mainly simple sugars and polymeric carbohydrates (hydrocolloid gums), the latter of which usually constitute 3% to 6% of the extract and heavily contribute to extract viscosity, while the balance is accounted for by a low percentage of moisture. Although the exact structure is not known, it is believed that the main polyphenolic pattern in quebracho tannins is represented by flavonoid analogues based on resorcinol A

25

- 4 -

and pyrogallol B rings as shown in Formula I below:



The second component of the reaction mixture is an aldehyde. A preferred material is formaldehyde which can be used in the form of a 37% active formaldehyde solution. This is also commercially available as formalin which is an aqueous solution of 37% formaldehyde which has been stabilized with from 6-15% methanol. Other commercial grades of formaldehyde and its polymers could be used. Such commercial grades include 44, 45 and 50% low-methanol formaldehyde, solutions of formaldehyde in methyl, propyl, n-butyl, and isobutyl alcohol, paraformaldehyde and trioxane. When using solid paraformaldehyde, care should be taken to ensure that it all dissolves.

Other aldehyde-containing or-generating reactants which can be used include organic chemical compounds which contain at least one aldehyde group therein, for example acetaldehyde, propionaldehyde, glycolaldehyde, glyoxylic acid and polyaldehydes (i.e., organic compounds having more than one aldehyde group in the compound) such as glyoxal and paraformaldehyde. Other suitable aldehyde reactants include aldehyde-generating agents i.e. known organic compounds capable of forming an aldehyde group in situ, such as melamine-formaldehyde monomeric products such as tri and hexa(methylol) melamine and the tri and hexa (C₁-C₃ alkoxymethyl)melamine. Such material can be formed by known conventional methods. The alkyl blocked derivatives are commercially available, are stable to self polymerization

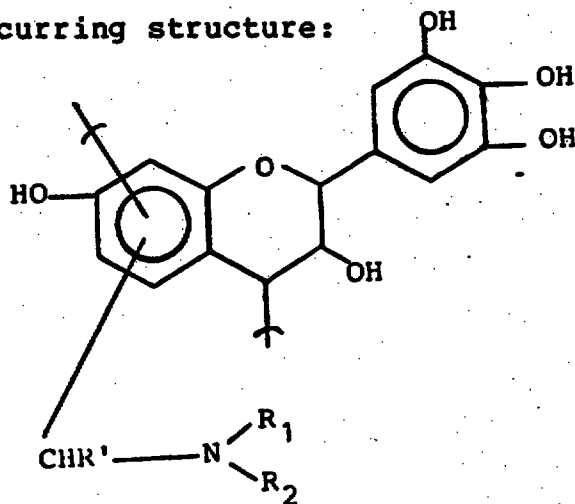
and are, therefore, preferred.

The third component for the reaction product is an amino compound which contains, or is capable of generating under the reaction conditions, a primary amino group, such as ammonia or a primary or secondary amine or amide compound. Preferred materials include primary amines such as monoethanolamine, methylamine and ethylamine. The primary amines are preferred since they are more reactive than secondary or tertiary amines.

10 It is necessary to react these three components under very controlled conditions, especially under an acidic condition where the pH is less than 7. Any acid can be used to obtain this condition; especially preferred are muriatic acid and acetic acid.

15 A further preferred material to be used in the reaction is an antifoamer material to prevent any foaming from taking place. Examples of these materials include silicon anti-foamers such as Silicone B made by Dow Chemical Co. Mineral seal oil and high molecular weight
20 alcohols can also be used.

The product obtained is believed to consist of a polymeric substance which has been modified by a "Mannich" reaction. In the Mannich reaction an aldehyde is condensed with an amino compound and an active
25 hydrogen supplied by the polyphenolic tannin. Although the structure of tannin is not completely known, it is believed the reaction product can be approximated by the following recurring structure:



where CHR' is the remainder of the aldehyde compound after the carbonyl oxygen has left and

R₁ and R₂ are independently hydrogen or organic moieties that were part of the original amino compound.

5 According to this theory the molecular weight of a repeating tannin unit is assumed to be approximately 300. The molar ratio of the primary amine to the tannin repeating unit is from 1.5:1 to 3.0:1.

 As the reaction between the three ingredients
10 proceeds under heated conditions, the extent of the reaction is controlled by monitoring the viscosity of the reaction mixture which is called the "intermediate viscosity". We have found that for any given reactant system involving these three components there is a relatively narrow range of
15 intermediate viscosity which determines the point at which the reaction should be terminated. We refer to this range as the "system key intermediate viscosity range". Once this range is reached, the reaction should be terminated, for example, by quenching and rapid external cooling. We have
20 found this intermediate viscosity has an effect on the final viscosity of the product at room temperature which in turn will affect the stability or shelf life of the product. By carefully controlling the intermediate viscosity for each given reactant system, the resultant product can be produced
25 which has a long shelf life. This intermediate viscosity range can, of course, readily be determined by carrying out trial runs, stopping the reaction over a wide range of different viscosities of the product and determining in each case the shelf life of the resulting product. From these
30 results the viscosity range which corresponds to a product with long shelf life can be found quite simply.

 In one embodiment where tannin is mixed with an amino compound such as monoethanolamine, it is desirable to also add an antifoam material after dissolving the tannin in the
35 water. The pH is maintained slightly acidic by adding an acid such as hydrochloric acid. After this initial addition

29

- 7 -

takes place, it is preferable to cool the material down and to then add the aldehyde such as formaldehyde so the reaction mixture is at a temperature of approximately 120-130°F (49-54°C). Although the reaction is exothermic, additional heat is added if necessary to maintain the reaction temperature at 150-200°F (66-93 °C) and more preferably at about 180°F (82°C).

If the reaction temperature is lower than about 150°F (66°C), the final product does not have high activity and is less effective. If the reaction temperature is much higher than about 200°F (93°C), the product ages too quickly and tends to gel and not have the desired long shelf life.

The extent of reaction is monitored by checking the viscosity. When the viscosity of this reaction mixture at 180°F (82°C) reaches a level of 38-40 centipoises, then the reaction is rapidly stopped. This is preferably done by using external cooling and by quenching the reaction mixture by adding water and additional acid so that the solids content is in the range of 40-45 wt. % and the pH is in the range of 2.3-2.6. By controlling the reaction so that it only proceeds to an intermediate viscosity of 38-40 cps (when measured at 180°F (82°C)) an excellent product using these reactants is obtained which will generally have a shelf life of 4 to 6 months.

If the reaction is quenched earlier at a lower intermediate viscosity, the final product is a less effective flocculant. Thus, the lower the intermediate and the subsequent final viscosity, the less effective will be the product. For example, when 700 ppm of a product with a final viscosity at 135.8 cps was added to flocculate a 500 ppm humic acid solution, the resulting supernatant had a poor transmittance of 73%. However, when the same amount of a product according to the present invention (as described in Example 1 below) with a final viscosity of 246 cp was used 90% supernatant transmittance was observed. A standard test for flocculating activity is to add humic acid to water in a controlled amount and to then add the proposed

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flocculating agent. The agent should precipitate the humic acid and leave a supernatant liquid which is clear. The degree of transmittance of light through the supernatant is measured and serves as an indicator of the effectiveness of the flocculating agent. The higher the transmittance, the more effective is the flocculating agent.

If the reaction mixture is quenched at a higher intermediate viscosity than 38-40 cps, the product does not normally remain liquid for the desired 4-6 months. For example, when a product is made from the reactants with an intermediate viscosity which is greater than approximately 40 cps, the final product usually has a shelf life of less than 4 months.

Thus, by varying the intermediate viscosity for each given reactant system and determining the effective shelf life, one can obtain a narrow range for the system key intermediate viscosity as shown above. For the above-described system the system key intermediate viscosity range is from about 38-40 cps. For other systems with other reactants the system key intermediate viscosity ranges will generally be within the range of 2-100 cps when measured at 180°F (82°C) on a Brookfield LVT viscometer.

The mole ratio of the primary amine to tannin repeating unit should be controlled. The primary amine content is referred to since this is the one that is the most reactive and it will readily take part in the Mannich reaction. Although secondary amines are operable and can be used, we much prefer primary amines and the following discussion will be in terms of these preferred primary amines. Assuming a repeating tannin unit with a molecular weight of 300 based on the polyphenolic constituent illustrated in Formula I above, the monoethanolamine to tannin repeating unit molar ratio of this embodiment is preferably 1.7:1 to 2.0:1 and more preferably 1.86:1, as illustrated by the reaction in Example 1. Reactions were run identically to the procedure in Example 1 except that

30

- 9 -

the monoethanolamine addition was increased so that the resulting primary amine:tannin molar ratio was in the range of 2.0-2.5:1. In Table 1 below are the results of a flocculating test using 500 ppm of a standard humic acid solution.

Table 1

<u>Amine:Tannin Mole Ratio</u>	<u>ppm Product Added to a 500 ppm Humic Acid Solution</u>	<u>% Transmittance of Supernatant</u>
1.86:1	700	90
2.00:1	700	84
2.25:1	700	81
2.50:1	700	73

This data shows the less effective flocculant obtained when the primary amine:tannin molar ratio is increased above the desired level of 2.0:1. If the primary amine:tannin molar ratio is below the preferred lower value of about 1.7:1, then the reaction product ages too quickly to be a useful, commercial product.

After the product has been made, the pH of the liquid should be adjusted to provide a long product shelf life. We have found that the higher the final product viscosity, the shorter will be the shelf life. In Table 2 below are the final product viscosities in centipoises when measured at 75°F (24°C) for product liquids made by the procedure in Example 1 and which have been adjusted to various pHs.

Table 2

<u>Final Product pH</u>	<u>Final Product Viscosity (cps)</u>
1.0	350
2.0	200
2.5	150
3.0	325
5.0	450
7.0	2,350
9.0	16,000
11.0	greater than 20,000

From this data it can be seen that the pH of the final product should be maintained at a value of less than 3.0; we have found an even more preferred range of from 2.3 to 2.6 for the products produced by the first 5 embodiment procedure.

The desired final product is a liquid which has a viscosity of less than 20,000 cps. If the viscosity over a relatively short period of time increases above 20,000 cps, then it is indicative that the material has formed an 10 undesirable gel which will not perform in a commercially acceptable manner. Eventually, all products made by reacting tannin with an amino compound and an aldehyde will increase in viscosity over time and finally gel.

In summary, the reaction should be conducted at an 15 acid pH of less than 7.0, the primary amine to tannin repeating unit molar ratio should be from 1.5-3.0:1, the reaction temperature should be from 150° to 200°F (66° to 93°C), the intermediate viscosity should be monitored and the reaction stopped when the narrow range is reached 20 which will be uniquely determined for each reactant system and which we refer to as the system key intermediate viscosity range, the pH for the final product should be adjusted to a value of less than 3.0 and more preferably 1.7-2.6 and the solids content of the liquid final product 25 should be adjusted, if necessary, to 20 to 60% by weight. By following this procedure a tannin based polymer compound can be produced which generally has a shelf life of greater than 3 months at ambient conditions.

In another embodiment for producing the tannin based 30 polymer compound it is possible to first react an aldehyde such as formaldehyde with an amino compound such as ammonium chloride to generate a primary amine compound in situ. Here the amines produced are a mixture of mono-, di-, and trimethylamines. A silicone antifoam material is added

35 and with stirring the reaction mixture is heated to, say,

140°F (60°C) for three hours. The material is then refluxed at a higher temperature of around 183°F (84°C) where it is maintained for an additional 3 hours. The amount of the desired primary reactive amine here is controlled by the reaction time. The longer the reaction time the less primary amine will be present in the solution because the less active secondary and tertiary amines will be formed. After this initial reaction has taken place, the reaction mixture can be cooled to a level of, say, 130°F (54°C) for subsequent mixing with the tannin compound. Note that because of the by-product acid produced when ammonium chloride reacts with the aldehyde, there is no need to add any additional acid to the reaction mixture to achieve the desired acid pH conditions.

In this second embodiment the tannin compound can be prepared in a separate reactor by mixing tannin with water and a silicone antifoaming agent. A preferred form of the tannin is a spray dried quebracho powder, sold as Mimosa Extract by Canadian Packers, Ltd. After the tannin has dissolved in the water at a relatively high temperature, say, 176-194°F (80-90°C) the aqueous tannin mixture is cooled to approximately 130°F (54°C). The methylamine/formaldehyde reaction mixture is added to the aqueous tannin mixture and the reaction is heated to about 183°F (84°C). The reaction is continued until the intermediate viscosity reaches the range of about 4-15 cps.

Upon achieving the desired extent of reaction, the mixture is quenched to room temperature by external cooling and the addition of water which adjusts the solids content in the range of about 28-32%. Since the acid producing ammonium chloride was used as the amino forming compound, it produced an acidic condition with pH of about 1.7-2.6. Thus it is not necessary in this case to add any

additional acid to adjust the final pH of the solution.

The following Examples further illustrate the present invention. It will be appreciated that trial runs were first conducted to establish the key intermediate viscosity range for the system.

Example 1

In this example the tannin based polymer compound was produced by using monoethanolamine as the amino compound and formaldehyde as the aldehyde.

10 A reactor containing 130.75 grams of deionized water was preheated to 150°F (66°C). Gradually 125.75 grams of Momosa Extract which is a spray-dried quebracho powder sold by Canadian Packers, Ltd. was gradually added while stirring. The temperature was maintained at about
15 130-140°F (54-60°C). After complete dissolution, the material was cooled to 110°F (43°C). Then 0.15 gram of the silicone antifoam Silicone B made by Dow Chemical was added.

To the aqueous tannin solution 47.65 grams of
20 monoethanolamine were added to yield a primary amine to tannin ratio of 1.86:1 while mixing; the temperature of the reaction mixture was allowed to rise to 130°F (54°C) and it was maintained at this temperature until all of the amine was added. In order to maintain the acid conditions
25 of the reaction mixture 80.0 grams of a 32% active hydrochloric acid was added to bring the pH in the range of 6.4 to 6.7 and the temperature was allowed to rise to 140°F (60°C). Upon forming this initial tannin/amine solution the mixture was cooled to 120°F (49°C).

30 Next, formaldehyde was added in the form of 62.70 grams of 37% active formaldehyde; the temperature during this addition was maintained between 120 and 130°F (49 and 54°C). As the formaldehyde was mixed with the previous solution the solution was heated to initiate the reaction.
35 The temperature was controlled so that it was not allowed

to go above about 180°F (82°C). As the reaction proceeded, the viscosity of the solution was monitored using a Brookfield LVT viscometer where the samples were measured at a temperature of about 178-180°F (81-82°C).

5 When the viscosity reading reached 38-40 cps, the desired degree of reaction was obtained. At this point the reaction material was quenched by external cooling and 45.20 grams of deionized water and 7.8 grams of muriatic acid was added to obtain a final pH of 2.4 and a solids
10 content of about 40.2% and a final viscosity of 246 cps.

The reaction product obtained was stored at ambient conditions and after six months it was still in a liquid form; it had not gelled solidified.

Example 2

15 A reactor was charged with 173.7 grams of 37% active formaldehyde, 38.50 grams of ammonium chloride and 0.07 grams of Silicone B. The reactor was equipped with an efficient condensor not under pressure and the temperature was slowly brought up to 140°F (60°C) while
20 stirring; this condition was maintained for 3 hours. Then the temperature was further increased to reflux conditions at a temperature of approximately 183°F (84°C) and reflux was maintained for an additional 3 hours. The initial reaction product consists of mono-, di-, and
25 tri-methylamines. The mixture was allowed to cool to below 130°F (54°C) so it could be subsequently added to an aqueous tannin mixture.

The aqueous tannin mixture was prepared in a separate stirred reactor by first preheating 104.85 grams
30 of deionized water to 176-194°F (80-90°C). To this stirred reactor 0.07 grams of the silicone antifoam was added along with 86.65 grams of Mimosa Extract which is a spray-dried quebracho powder. After the tannin material had dissolved
35 in the water the reactor was cooled to below 130°F (54°C).

Then the methylamine/formaldehyde solution obtained in the first reactor was slowly added to this aqueous tannin solution and the mixture was heated to about 185°F (85°C). The reactor is maintained at this temperature until the intermediate viscosity reached approximately 5.3 cps as measured by a Brookfield LVT viscometer at 185°F (85°C). After the desired intermediate viscosity was obtained, the reaction mixture was quenched by cooling it to room temperature and by adding 96.15 grams of deionized water which adjusted the solids content in the range of 28-32 weight percent.

The final reaction product had a solids content of 29.4%, a viscosity of 20 cps at room temperature and a pH of 1.9. It has been stored at ambient conditions for over five months without gelling or solidifying.

Example 3

The reaction products according to the present invention as made in Examples 1 and 2 were tested along with other flocculants, namely alum and ferric chloride (FeCl₃) in the treatment of river water to remove solids. The water employed was from the Yadkin River. The results are set forth in Table 3.

Table 3

	<u>Treatment</u>	<u>Dosage(ppm)</u>	<u>Turbidity (NTU)</u>	<u>Color (APHA UNITS)</u>
25	None - Control	-	17	50
	Alum	1	14	20
	FeCl ₃	1	17	30
	Example 1	6.8	8	less than 1
30	Example 2	9.6	7	2

The data in Table 3 shows that the products made according to the present invention substantially reduce the turbidity (in nephelometric turbidity units) from 17 down to 7 or 8. Similarly, the colour in APHA (American Public Health Association) units (which are based on a Pt-Co standard) is reduced from 50 to 2 and lower.

Example 4

The reaction products according to the present invention as made in Examples 1 and 2 where tested to remove humic acid from water. The humic acid was present in an amount of 500 ppm. The results are set forth in Table 4.

Table 4

<u>Treatment</u>	<u>Product Dosage (ppm)</u>	<u>% Transmittance of Wastewater Supernatant</u>
None	-	0
Product of Example 1	500	71
	800	90
	1000	90
Product of Example 2	500	73
	800	93
	1000	95

The data in Table 4 illustrates the significant flocculating effect obtained by these reaction products in removing the humic acid from the water at relatively low concentrations.



34

- 16 -

CLAIMS

1. A method of forming an aqueous solution of a tannin based polymer which comprises heating an aqueous mixture of a tannin, an amino compound which contains, or is capable of generating under the reaction conditions, a
5 primary amino group, and an aldehyde or a compound which generates an aldehyde group under the reaction conditions, under acidic conditions, the molar ratio of the primary amino groups of the amino compound to the tannin repeating unit being from 1.5:1 to 3.0:1, at 150°-200°F (66°-93°C)
10 until the reaction product which forms has a viscosity which is within the key intermediate viscosity range for the reaction system, said range being that for the said system which permits the resulting product to have desired shelf-life, and (c) terminating the reaction when the
15 viscosity has reached the condition specified above and, if necessary, adjusting the solids content of the liquid to 20 to 60% by weight and the pH to a value of less than 3.0.
2. A method according to claim 1, wherein the key
20 intermediate viscosity range is from 2 to 100 cps when measured at 130°F (82°C) on a Brookfield LVT viscometer.
3. A method according to claim 1 or 2, wherein the amino compound is monoethanolamine.
4. A method according to claim 1 or 2, wherein the
25 amino compound is methylamine, dimethylamine or trimethylamine or a mixture thereof.
5. A method according to any one of claims 1 to 4, wherein the aldehyde is formaldehyde.
6. A method according to any one of claims 1 to 5,
30 wherein the mixture is heated to a temperature of 175° to 185°F (79° to 85°C).
7. A method according to any one of claims 1 to 6, wherein the amino compound is an amine and the primary amine group to tannin repeating unit molar ratio is from
35 1.7:1 to 2.0:1.



- 17 -

8. A method according to any one of claims 1 to 7, wherein the tannin is a quebracho powder.

9. A method according to any one of claims 2 to 8, wherein the reaction temperature is 175-185°F (79-85°C), the viscosity is 38-40 cps, the final solids content is 35 to 45 weight % and the pH is 1.7 to 2.6.

10. A method according to claim 9, wherein the solids content in step (c) is adjusted to 40 to 45% by weight.

11. A method according to claim 9 or 10, wherein the pH of the reaction product in step (c) is adjusted to 2.3 to 2.6.

12. A method according to any one of claims 2 to 5, wherein the reaction temperature is 175-185°F (79-85°C), the viscosity is 4-15 cps, the final solids content is 38-32 weight percent and the pH is 1.7 to 2.6.

13. A method according to claim 12, wherein the pH is about 1.9.

14. A method according to claim 1 substantially as described in any one of the Examples.

15. An aqueous solution of a tannin based polymer whenever formed by a process as claimed in any one of the preceding claims.

16. A process for treating wastewater by the addition of a flocculant, the flocculant being the aqueous solution of a tannin based polymer as claimed in claim 15.
