



(21) (A1) **2,325,433**  
(86) 1999/03/02  
(87) 1999/09/30

(72) CROFT, ALAN P., US

(71) THE DOW CHEMICAL COMPANY, US

(51) Int.Cl.<sup>6</sup> D21C 5/02, D21C 9/08, D21H 21/02

(30) 1998/03/25 (09/047,803) US

(54) **PROCEDE D'INHIBITION DU DEPOT DE POIX BLANC AU  
COURS DE LA PRODUCTION DE PAPIER**

(54) **METHOD FOR INHIBITING THE DEPOSITION OF WHITE  
PITCH IN PAPER PRODUCTION**

(57) L'invention concerne un ou des composé(s) d'éthylèneamine ou des mélanges de ceux-ci, utilisés en quantité efficace pour réduire ou inhiber le dépôt de poix blanc sur l'équipement de fabrication de papier, pendant le traitement de recyclage d'un papier couché.

(57) Ethyleneamine compound(s), or mixtures thereof, are used in effective amounts to reduce or inhibit the deposition of white pitch on the paper making equipment during the processing to recycle coated paper.

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> :	A1	(11) International Publication Number:	WO 99/49128
D21C 5/02, 9/08, D21H 21/02		(43) International Publication Date:	30 September 1999 (30.09.99)

(21) International Application Number:	PCT/US99/04792		
(22) International Filing Date:	2 March 1999 (02.03.99)		
(30) Priority Data:	09/047,803	25 March 1998 (25.03.98)	US
(71) Applicant:	THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Midland, MI 48674 (US).		
(72) Inventor:	CROFT, Alan, P.; 325 Petunia, Lake Jackson, TX 77566 (US).		
(74) Agent:	KARADZIC, Dragan, J.; Patent Dept., B-1211, 2301 N. Brazosport Boulevard, Freeport, TX 77541 (US).		
		Published	<i>With international search report.</i>

(54) Title: METHOD FOR INHIBITING THE DEPOSITION OF WHITE PITCH IN PAPER PRODUCTION

## (57) Abstract

Ethyleneamine compound(s), or mixtures thereof, are used in effective amounts to reduce or inhibit the deposition of white pitch on the paper making equipment during the processing to recycle coated paper.

**METHOD FOR INHIBITING THE DEPOSITION OF WHITE PITCH  
IN PAPER PRODUCTION**

The present invention relates to the inhibition of  
5 the deposition of white pitch in paper production.

Paper manufacture, in the simplest sense, involves  
producing a pulp from wood, slurring the pulp and water,  
and forming a pulp mat, which is pressed and dried to form  
10 paper. In the critical forming step, the pulp/water  
slurry (furnish) is formed as a mat on the wire web of the  
paper machine. Excess water and fines (white water) pass  
through the mat on the wire and are recycled. The formed  
web goes forward into the press and dryer section of the  
15 machines where the mat becomes paper.

Broke paper is the term used in the paper industry to  
describe the paper which does not meet specifications and  
for that reason cannot be sold. This paper is usually  
20 recycled internally at the mill to recover fibers but it  
may also be sold to other mills as a source of fiber. The broke  
paper may be coated, the coating being applied to  
the base sheet of paper as it is manufactured. The broke  
paper which is coated is referred to as coated broke  
25 paper. Waste paper is the term used in the paper industry  
to describe paper which has been utilized by a consumer.  
It is often termed "post consumer waste." This paper is  
often collected and recycled at a mill to recover fibers.  
The waste paper may be coated, the coating being applied  
30 to the base sheet of paper as it is manufactured. The  
waste paper which is coated is referred to as coated waste  
paper. Coated paper that is recycled can be broke or  
waste paper. In recent years many paper mills have  
experienced problems with the recycling of coated paper

because the coatings introduce materials which normally would not be present in the original stock of fibers used to manufacture the base paper sheet.

5        The coatings normally comprise various pigments and binders. Typical pigments used include many types of clay, calcium carbonate, titanium dioxide, and other specialty fillers. The problems of white pitch are thought to be mainly caused by the binders which include  
10      latex polymers derived from styrene-butadiene and polyvinyl acetate resins and natural binders such as starch.

White pitch problems have been known for some time in  
15      the paper producing industry. White pitch is sticky, light gray substance which is found as a deposit on metal surfaces in the in the wet-end, forming press, or dryer sections of the paper machine. It is termed "white" to distinguish it from the brown or black pitch, which  
20      results from materials contained in the wood. White pitch is also found in the white water system. At times the pitch deposits carbonize to give black deposits in the dryer section of the paper machine. The white pitch problem has been shown to be caused by the relatively high  
25      use of coated paper in the furnish of mills experiencing the problem. When coated paper is re-pulped, the clay or minerals and the latex in the coatings do not readily disperse into the pulp but form agglomerations, which result in white pitch. White pitch can coat the equipment  
30      or form defects in the paper if it travels into the paper machine with the pulp. High machine downtime, frequent cleaning, paper sheet defects such as holes, and increased number of sheet breaks are costly problems associated with white pitch deposits. Equipment clean up is quite

involved because deposits can be found on the foils, table rolls, vacuum boxes, dryer cans and dryer felts, and throughout the press felts.

5        Various solutions have been suggested for dealing with the white pitch problem. Several deposit control chemicals are currently being used or evaluated by the paper industry. By trapping and dispersing the small latex particles in the sheet, the white pitch problem can  
10      be controlled. More specifically, the latex particles should be attached to the fibers immediately passing through the re-pulper. At this point the latex particles are small and anionic, and therefore, they can exit the system as part of a sheet. Due to the anionic character  
15      of both the latex particles and the fibers, an additive having low molecular weight and high cationic charge is best suited for this purpose. However, the additive alone may not be sufficient to contain the latex particles in the paper sheet and the use of a retention aid compatible  
20      with the additive may be important for successful control of white pitch.

25       Synthetic polymers are the most successful known antideposition additives for white pitch. They are highly cationic, enabling them to create a strong electrostatic bond between the fibers, the latex particles and the additive. Once bonded, the fiber will carry the latex particles through the mill, with the help of a retention aid, and the particles will become part of the finished  
30      paper. Medium molecular weight polyglycol, amine/glycol or polyethyleneimine polymers have been shown to be useful in reducing white pitch.

Some of the methods for treating white pitch problems are described in documents below.

U.S. Patent No. 5,131,982 (Michael R. St. John) 5 describes the use of DADMAC containing polymers and copolymers to treat cellulose fibers recycled from coated broke recovery to make them suitable for making paper.

U.S. Patent No. 4,997,523 (Pease et al) describes the 10 use of a tetrafunctional alkoxylated diamine in combination with a phosphate compound, phosphonate compound or phosphoric acid to minimize the deposition of white pitch on paper making equipment.

15 U.S. Patent No. 4,643,800 (Maloney et al) describe the use an oxyethylene glycol nonionic surfactant in which one end hydroxyl group has been substituted with an aliphatic or alkylaromatic group and the other end hydroxyl group has been replaced with a polyoxypropylene 20 group or a benzyl ether group in combination with a medium molecular weight (500-50,000) polyelectrolyte dispersant to remove and disperse contaminants from secondary fiber during re-pulping.

25 There are several disadvantages of the use of polymers to control white pitch. Polymers are not generally cost efficient. For example, polyethyleneimine (PEI), a tertiary amine polymer, is an effective white pitch control additive yet it is quite costly to use. 30 Also, as the length of a polymer increases the chance of the polymer breaking down and releasing the latex particles also increases. Polymers can even cause deposits due to the difficulty in controlling the polymer from attaching latex particles to other latex particles.

WO 99/49128

PCT/US99/04792

Moreover, polymers are not generally water soluble which limits their applicability.

There are other solutions used for control of white pitch. Talc was commonly used in the past and is still sometimes used to control deposits. As a surface-active filler, talc acts to control deposits by drying the area around the pitch particle so that it cannot attach to the paper making equipment. However, this offer only a temporary solution to the pitch problem which reappears as the process continues. Talc does not bind the latex particles to the fibers, and therefore when exposed to shear, new tacky areas appear causing deposits. Also, additives which react with the surface of the pitch particle to render it less tacky (detackifiers) offer temporary solution to controlling white pitch. As with talc, this solution fails when exposed to shear. Both talc and tackifiers can be effective only when used with a good retention aid. The objective of retention aids is to cause latex particles to repel each other which sends them through white water. Eventually, pitch is deposited on the pump impellers, tank walls, and agitators.

It is evident that there is a need in paper making industry for an improved method of controlling the white pitch problem experienced with the recycling of coated paper.

Surprisingly, it has now been found that the deposition of white pitch on the paper making equipment can be inhibited in a simple and effective manner by the addition of ethyleneamine compounds to the coated paper during the re-pulping operation.

111 27.01.2000

Accordingly, the present invention concerns a process for reducing or inhibiting the deposition of white pitch on paper making equipment during the processing of the recycled coated paper which method comprises adding to the 5 coated paper during re-pulping an effective amount for reducing the deposition of white pitch of at least one ethyleneamine compound.

The term ethyleneamine as used in the present 10 invention means an amine having at least one ethyleneamine unit or repeating ethyleneamine units. An ethyleneamine unit is  $-(CR_2-CH_2-NH)-$  wherein each R is independently selected from H or an alkyl (straight, branched or cyclic) group. R is preferably H. When R is alkyl group, it is 15 preferred that the alkyl group contains from about 1 to about 10 carbon atoms. Ethyleneamines have at least two amine groups, which groups are primary or secondary amine groups. Tertiary amine groups may also be present in ethyleneamines.

20

Examples of ethyleneamines useful in the present invention include, but are not limited to, ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, piperazine, aminoethylpiperazine, 25 ethyleneamine mixtures such as mixtures of ethyleneamine oligomers having an average molecular weight of about 250-300 commercially available from The Dow Chemical Company under the trade designation Ethyleneamine E-100, and other mixtures thereof. In the case of ethyleneamines having 30 isomers, one isomer or a mixture of isomers is suitably used in the practice of the invention.

The concentration of the ethyleneamine compound(s) which has been found to be effective for reducing or inhibiting the deposition of white pitch is typically in the range of from 10 ppm to 5000 ppm, preferably from 100 5 ppm to 2500 ppm, more preferably from 500 ppm to 1500 ppm, of the ethyleneamine compound based upon total paper solids.

It should be understood that since the processing of 10 the recycled coated paper may result in generation of problems and paper defects other than white pitch, the present invention may be used in conjunction with other additives commonly used in paper making process such as retention aids and conditioners.

15

The examples which follow are given to illustrate the invention and should not be interpreted as limiting it in any way. Unless stated otherwise, all parts and percentages are given by weight.

20

### Examples

The effectiveness of the ethyleneamine compounds to inhibit or reduce the deposition of white pitch was 25 evaluated in a test which measures the depositable material in coated paper broke. The test procedure was based on "TAPPI Useful Method 223: Determination of Depositable Material in Pulp and the Evaluation of 30 Chemical Deposit Control Agents" method, published by the Technical Association of the Pulp and Paper Industry in "TAPPI Useful Methods," pp. 30-32, 1991. In this method, two stainless steel plates were made to vibrate in agitated solution of re-pulped coated paper and the 35 additive to be tested. The pitch was measured by the net

43087

127-01-00

weight gain of the plates. Successful deposit control additives give a zero weight gain on the plates.

A Waring commercial blender was used to re-pulp the  
5 coated paper. The test apparatus comprised: (iv) a 4  
liter polypropylene beaker; (ii) an overhead stirrer with  
a stainless steel shaft and propeller suspended in the  
beaker; (iii) a laboratory vibrating device, clamped to a  
stainless steel shaft [0.25 inch (0.53 cm) in diameter]  
10 with one end drilled and tapped 0.5 inch (1.27 cm) deep  
for an 0.25 inch (0.53 cm) machine screw, suspended in the  
beaker adjacent to the overhead stirrer; and (iv) two type  
304 stainless steel plates [25 mils (0.635 mm) thick],  
trimmed to size 2.75 X 3.75 inches (6.98 X 9.52 cm), and  
15 drilled on one end for an 0.25 inch (0.53 cm) machine  
screw attached to the stainless steel shaft with clamped  
vibrating device. Standard laboratory glassware and  
equipment were used for other experimental operations.

20 A 2.5 percent slurry was prepared using the  
commercial blender in the following manner. Distilled  
water (1800 ml) and the required amount of the additive  
were mixed in the blender. Shredded coated paper (45 g)  
was added and allowed to soak for 10 minutes. At the end  
25 of the 10 minute period, the mixture was blended for 75  
seconds on the low setting. After blending, the mixture  
was poured into the 4 liter polypropylene beaker.

30 The stainless steel plates were scrubbed with diatomaceous  
earth (Celite 545), rinsed with distilled water and placed  
in laboratory oven. After removal from the oven, the  
plates were cooled to room temperature in a desiccator,  
weighed and attached to the shaft with the clamed

43087

11 27-01-00

vibrating device. The stainless steel shaft and the overhead stirrer were immersed in the slurry

WO 99/49128

PCT/US99/04792

transferred to the beaker. The stainless steel shaft was then adjusted so that the plates did not interfere with the operation of the overhead stirrer. The overhead stirrer was started and the speed increased until the 5 slurry moved slowly over the plates. Once the stirring velocity was stabilized, the vibrating device was started. After 30 minutes, both the overhead stirrer and the vibrating device were shut off. The plates were detached from the shaft, rinsed with distilled water and dried in 10 the laboratory oven. After removal from the oven, the plates were cooled to room temperature in a desiccator, weighed and the net weight change for the set was recorded.

15        Ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA) and Ethyleneamine 100 (EA-100) were tested at the dose levels of 500, 1000 and 1500 ppm in the above described test procedure (using the aforementioned apparatus) three 20 times at each dose level and the average pitch deposited was calculated. The concentrations of the additives were based upon the total coated paper solids in the slurry. Additionally, a known polymeric antideposition additive was tested as a comparative example in the same way as the 25 ethyleneamines: polyethyleneimine of 1800 molecular weight (PEI). The results were given in Table I below.

TABLE 1.  
Results for the Evaluation of Deposit Control  
Additives

Example	Additive	Avg. Net Pitch at 500 ppm	Avg. Net Pitch at 1000 ppm	Avg. Net Pitch at 1500 ppm
1	EDA	0.0002	0.0003	0.0004
2	DETA	0.0002	0.0005	0.0003
3	TETA	0.0003	0.0001	0.0003
4	TEPA	0.0003	0.0003	0.0000
5	E-100	0.0001	0.0000	0.0000
C-1	None	0.0012	0.0012	0.0012
C-2	PEI	0.0001	0.0001	0.0001

Note: Examples C-1 and C-2 are not examples of the  
5 present invention.

As can be seen from the data provided in Table 1, all  
tested ethyleneamine compounds reduced drastically the  
amount of pitch deposited. E-100 demonstrated to be the  
10 most effective in controlling pitch since it reduced the  
deposits by 100 percent at the 1000 ppm and 1500 ppm dose  
levels. On the other hand, the known pitch control  
polymer additive (PEI) reduced the deposits by only 92  
percent at the same dose levels.

43087

11:27:01:00

WHAT IS CLAIMED IS:

1. A process for reducing the deposition of white pitch on the paper making equipment during the processing of the recycled coated paper which method comprises adding to the coated paper an effective amount for reducing the deposition of white pitch of at least one ethyleneamine compound.

10 2. The process of Claim 1 wherein the ethyleneamine compound has at least one -(CR<sub>2</sub>-CR<sub>2</sub>-NH-) unit wherein each R is independently selected from H or an alkyl group containing from 1 to 10 carbon atoms.

15 3. The process of Claim 2 wherein the ethyleneamine compound is selected from the group consisting of ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, mixtures of ethylenamine oligomers having a average molecular weight of 60-500, and mixtures thereof.

20 4. The process of Claim 1 or Claim 2 wherein the ethyleneamine compound is added to the coated paper in an amount of from 10 ppm to 5000 ppm based upon total coated paper solids.

25 5. The process of Claim 4 wherein the ethyleneamine compound is added to the coated paper in an amount of from 100 ppm to 2500 ppm based upon total coated paper solids.

30 6. The process of Claim 5 wherein the ethyleneamine compound is added to the coated paper in an amount of from 500 ppm to 1500 ppm based upon total coated paper solids.