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(54) **USE OF CELLULOSE NANOCRYSTALS AS A CORROSION INHIBITOR**

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(57) **ABSTRACT**

The present invention relates to the use of charged cellulose nanocrystals as a corrosion inhibitor. According to one aspect, there is provided a corrosion inhibitor comprising of a plurality of charged cellulose nanocrystals fibrils. There is further provided a process for inhibiting corrosion of metal equipment where water can reside. According to a further aspect, the process includes adding an effective corrosion inhibiting amount of acid-form the cellulose nanocrystals. According to another aspect, the process includes selectively causing a first set of the cellulose nanocrystals to be negatively charged. The first set of the cellulose nanocrystals so charged function as an anodic corrosion inhibitor. The process includes selectively causing a second set of the cellulose nanocrystals to be positively charged. The second set of the cellulose nanocrystals so charged functions as a cathodic corrosion inhibitor.

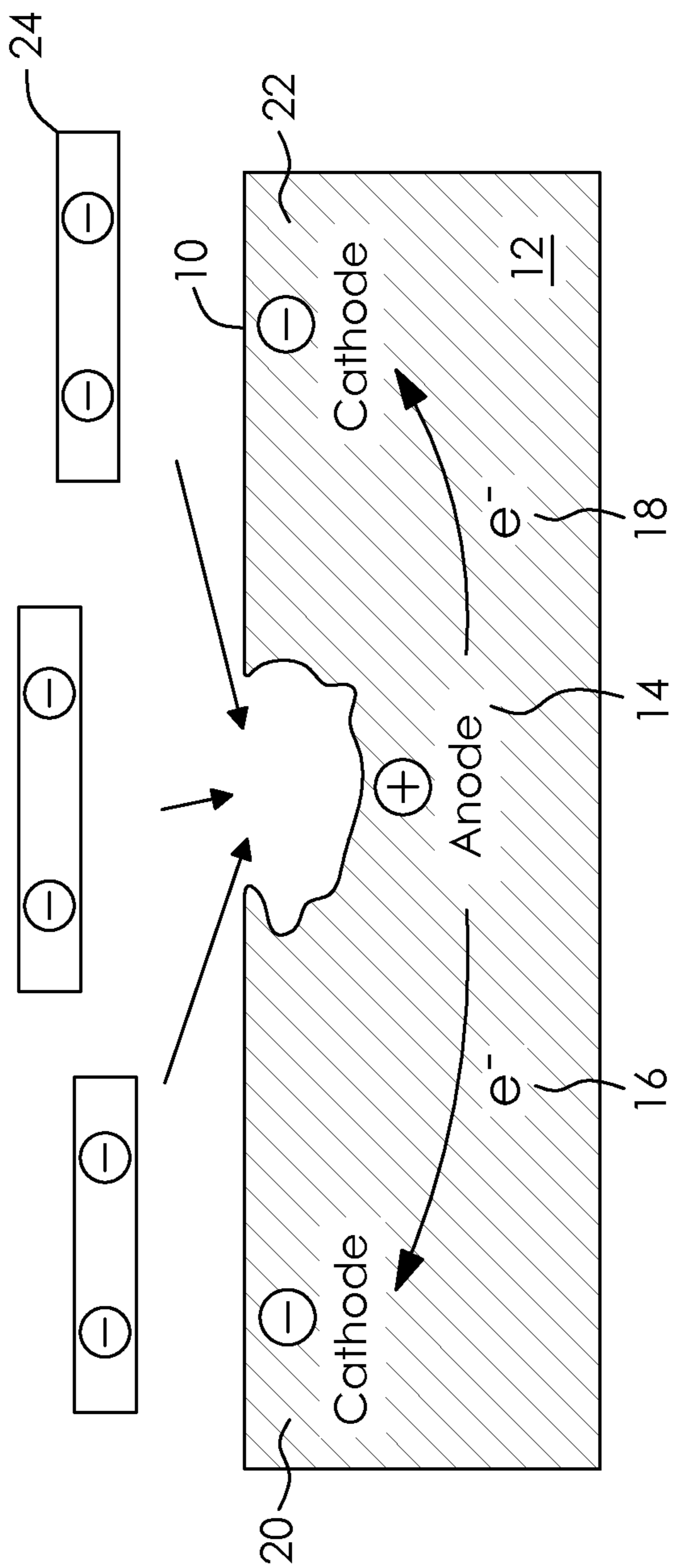


FIG. 1

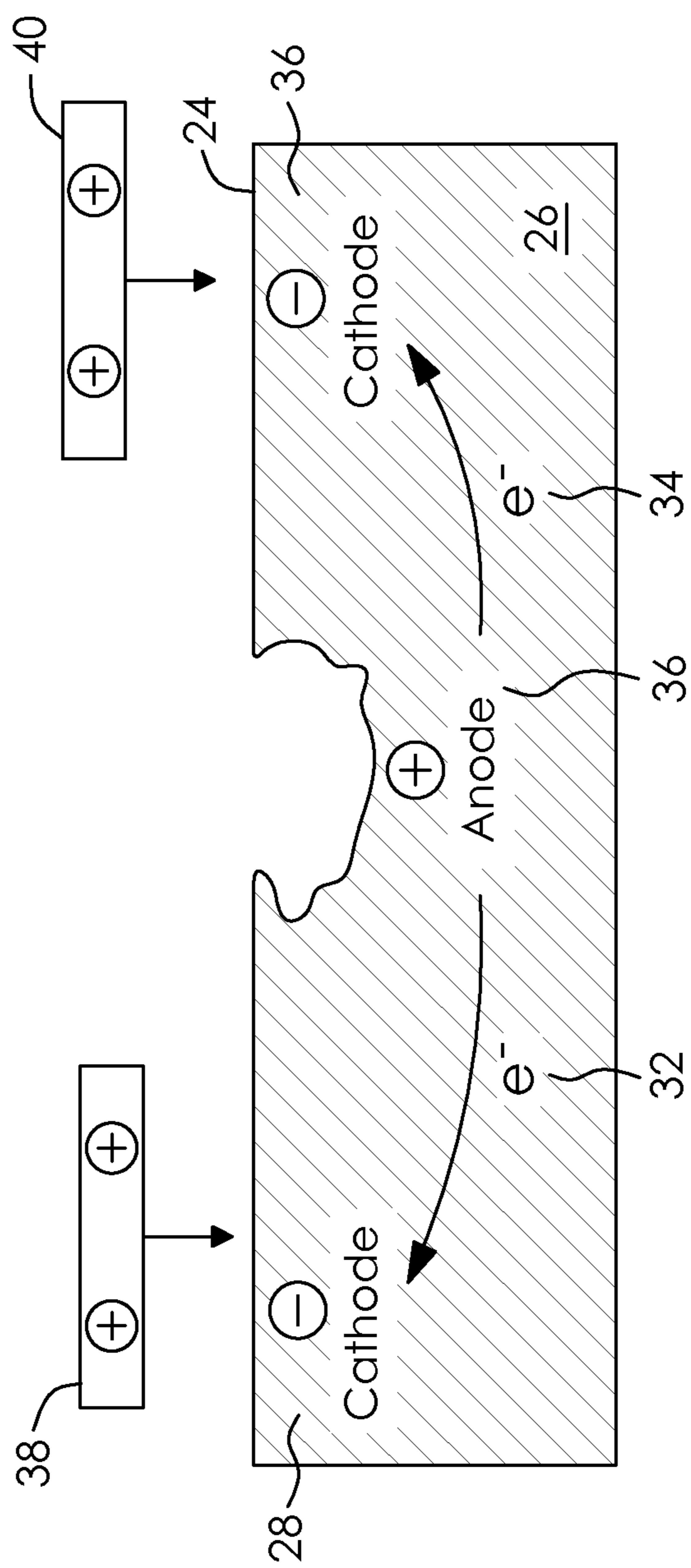


FIG. 2

USE OF CELLULOSE NANOCRYSTALS AS A CORROSION INHIBITOR

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of provisional application No. 61/668,001 filed in the United States Patent and Trademark Office on Jul. 4, 2012, the disclosure of which is incorporated herein by reference and priority to which is claimed.

FIELD OF THE INVENTION

[0002] The present invention relates to cellulose nanocrystals. In particular, the invention relates to the use of cellulose nanocrystals as a corrosion inhibitor.

DESCRIPTION OF THE RELATED ART

[0003] It is known per se to use azole compounds to inhibit corrosion. For example, U.S. Pat. No. 4,134,959 to Menke et al. provides a composition and method for inhibiting corrosion. The composition consists essentially of an azole and a water-soluble phosphate in an effective combination to inhibit corrosion in both ferrous and non-ferrous metals.

[0004] However, azole compounds are relatively expensive. There is accordingly a need for an effective corrosion inhibitor that is less costly.

BRIEF SUMMARY OF INVENTION

[0005] It is object of the present invention to provide, and the present invention discloses herein, a cellulose nanocrystal corrosion inhibitor that overcomes the above disadvantages.

[0006] There is accordingly provided the use of charged cellulose nanocrystals as a corrosion inhibitor.

[0007] There is also provided a corrosion inhibitor comprising a plurality of charged cellulose nanocrystals.

[0008] There is further provided a process for inhibiting corrosion of metal equipment where water can reside. The process includes adding an effective corrosion inhibiting amount of charged cellulose nanocrystals. According to one aspect, the process includes causing the cellulose nanocrystals to be negatively charged. The cellulose nanocrystals so charged function as an anodic corrosion inhibitor.

[0009] According to another aspect, the process includes causing the cellulose nanocrystals to be positively charged. The cellulose nanocrystals so charged functions as a cathodic corrosion inhibitor.

[0010] According to a further aspect, the process includes selectively causing a first set of the cellulose nanocrystals to be negatively charged. The first set of the cellulose nanocrystals so charged function as an anodic corrosion inhibitor. The process includes selectively causing a second set of the cellulose nanocrystals to be positively charged. The second set of the cellulose nanocrystals so charged functions as a cathodic corrosion inhibitor.

BRIEF DESCRIPTION OF DRAWINGS

[0011] The invention will be more readily understood from the following description of preferred embodiments thereof given, by way of example only, with reference to the accompanying drawing, in which:

[0012] FIG. 1 is a diagrammatic view of a corroding metal having ionic components including positively charged ionic

components, and a plurality of negatively charged cellulose nanocrystals being attracted to said positively charged ionic components; and

[0013] FIG. 2 is a diagrammatic view of a corroding metal having ionic components including negatively charged ionic components, and a plurality of positively charged cellulose nanocrystals being attracted to said negatively charged ionic components.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0014] Cellulose nanocrystals are typically in the form of rod shaped fibrils or needles. The fibrils may, for example, have a length/diameter ratio of about 20 to 200, a diameter preferably less than about 60 nm, a diameter more preferably in the range of 4 nm to about 15 nm, and a length of about 150 nm to about 350 nm. Cellulose nanocrystals as referred to herein may alternatively be referred to as cellulose nanocrystals (trademark), cellulose nanofibres or cellulose whiskers. Dried forms of cellulose nanocrystals may be obtained via acid hydrolysis, as for example set out in International Patent Publication No. WO 2010/066036 A1 to Beck et al., the disclosure of which is incorporated herein by reference. Cellulose nanocrystals may be purchased at CelluForce Inc., which has an office at 625 President Kennedy, Montreal, Québec, H3A 1K2.

[0015] According to one aspect, it has been discovered that cellulose nanocrystals are an effective corrosion inhibitor. Although this invention is not restricted to any one production method, one preferred embodiment of this invention is to use cellulose nanocrystals produced as described in International Patent Publication No. WO 2010/066036 A1 by Beck et al. According to one aspect, it has been found that the acid-formed cellulose nanocrystals are effective corrosion inhibitors.

[0016] When cellulose nanocrystal fibrils are caused to be charged, the cellulose nanocrystals so charged are attracted to oppositely charged ionic components of a corroding metal surface. The fibrils as a result form a coating around the ionic components of the metal surface and prevent electrochemical reactions from driving the corrosion process thereby. Cellulose nanocrystals are effective since the very small scale needle-like crystals have a very large surface area for a given weight. Because of this property, only small concentrations of cellulose nanocrystals are needed to form thin coatings that inhibit corrosion.

[0017] FIG. 1 shows corrosion of a surface 10 of a metal 12 occurring at a positively charged anode or anodic site 14. The corrosion process can be driven by an oxidizer such as oxygen which draws electrons 16 and 18 to cathodic sites 20 and 22, leaving the separate anodic site 14 with a positive charge. Charged cellulose nanocrystals, in this example negatively charged cellulose nanocrystals 24 are attracted to the anodic site 14, moving down a potential gradient. The charged cellulose nanocrystals accumulate and coat the anode, thus inhibiting corrosion of the metal 12. In this way, the cellulose nanocrystals 24 act as an anodic corrosion inhibitor. In this example, each cellulose nanocrystal 10 has two negative charges, though this number is not strictly required and other numbers of negative charges are possible.

[0018] By analogy, a different form of cellulose nanocrystals may be created by chemical reaction, such as treatment with a cationic polymer, to be positively charged and thus act as a cathodic corrosion inhibitor. FIG. 2 shows corrosion of a

surface **24** of a metal **26** occurring at negative charged cathodes or cathodic sites **28** and **30**. In this example, oxygen draws electrons **32** and **34** to sites **28** and **30**, respectively, leaving a separate anodic site **36** with a positive charge. Charged cellulose nanocrystals, in this example positively charged cellulose nanocrystals **38** and **40** are attracted to the cathodic sites **28** and **30**, respectively. The positively charged cellulose nanocrystals in this case accumulate and coat the cathodic sites, thus inhibiting the corrosion process by inhibiting access to the cathodic sites. In this manner, the cellulose nanocrystals **38** and **40** thus act as a cathodic corrosion inhibitor. In this example, each cellulose nanocrystal has two positive charges, though this number is not strictly required and other numbers of negative charges are possible.

[0019] A series of corrosion tests were performed the results of which are shown in Table 1 set out below.

TABLE 1

Coupon Weight Loss in mils per year (mpy)				
	Salt Solution (control)	Salt Solution with Cellulose Nanocrystals (dried-form, Na-CNC) added to the solution	Salt Solution with Phosphoric Acid (control)	Salt Solution with Phosphoric Acid and Cellulose Nanocrystals (dried-form, Na-CNC) added to the solution
Steel Coupons (S)	S1 = 1.2 mpy	S2 = 1.7 mpy	S5 = 14.4 mpy	S6 = 12.0 mpy

[0020] Corrosion rates were measured by immersing coupons of carbon steel 4130 (S) in typical seawater compositions and measuring the loss of mass due to corrosion after 33 days. The coupons were left at ambient temperature and remained sealed within jars.

[0021] The mass of the coupons were determined before and after the 33 day period to an accuracy of $\pm 10^{-5}$ grams. Mils per year (mpy) corrosion rates were obtained thereby following the protocol outlined in the NACE International Corrosion Engineers Reference Book, 2nd Edition, at set out on pages 78 and 79 therein. This book may be obtained at NACE International, which has an address at 1440 South Creek Drive, Houston, Tex., 7084-4906, USA.

[0022] Coupon S1 was tested in a jar containing a control test salt solution comprising 500 grams of water and 25 grams of sea salt, as seen in table 2. The sea salt used in this example was Agenco(trademark) sea salt, which may be purchased at Whole Foods

[0023] Market IP. L.P., having an address at 2285 W 4th Ave, Vancouver, British Columbia, Canada. This resulted in a corrosion rate of 1.2 mpy.

TABLE 2

Mass of Chemicals in Formulation (grams)				
	Water (grams)	Sea Salt (grams)	Phosphoric Acid (grams)	Cellulose Nanocrystals (grams)
Salt Solution (control, coupon S1)	500	25	0	0
Salt Solution with Cellulose	500	25	0	34

TABLE 2-continued

Mass of Chemicals in Formulation (grams)				
	Water (grams)	Sea Salt (grams)	Phosphoric Acid (grams)	Cellulose Nanocrystals (grams)
Nanocrystals (dried-form, Na-CNC) added to the solution (coupon S2)				
Salt Solution with Phosphoric Acid (control, coupon S3)	500	25	60	0
Salt Solution with Phosphoric Acid and Cellulose	500	25	60	34

TABLE 2-continued

Mass of Chemicals in Formulation (grams)				
	Water (grams)	Sea Salt (grams)	Phosphoric Acid (grams)	Cellulose Nanocrystals (grams)
Nanocrystals (dried-form, Na-CNC) added to the solution (coupon S4)				

[0024] Coupon S2 was tested in a jar containing 500 grams of water, 25 grams of sea salt and 34 grams of cellulose nanocrystals, as seen in Table 2. The cellulose nanocrystals added to the jar throughout the testing were in dried solid form in this example. The cellulose nanocrystals had originally been extracted through acid hydrolysis and then their proton counterions were replaced with monovalent cationic counterions to obtain the dried solid form that was used for the testing. In this example, the monovalent cationic counterions are sodium ions. The cellulose nanocrystals were thus sodium-form in this example (Na-CNC). However, other forms of monovalent cationic counterions may be used, such as K^+ , Li^+ , NH_4^+ and tetraalkylammonium (R_4N^+), protonated trialkylammonium (HR_3N^+), protonated dialkylammonium (H_2RaN^+), and protonated monoalkylammonium (H_3RN^+) ions for example.

[0025] The corrosion rate for coupon S2 was 1.7 mpy, which is over 40% higher compared to the corrosion rate of steel with just salt water. It was thus found that solid, dried form cellulose nanocrystals (Na-CNC), when added to the salt solution, appears to increase corrosion.

[0026] It was next desired to perform testing with acid-form, or charged, cellulose nanocrystals. It is known that dried, solid-form cellulose nanocrystals stabilized with monovalent cationic counterions can be converted to acid-form cellulose nanocrystals by adding acid to said dried, solid-form cellulose nanocrystals. Dried, solid-form cellulose nanocrystals stabilized with monovalent cationic counterions may be converted to acid-form cellulose nanocrystals by adding acid to said dried, solid-form cellulose nanocrystals.

[0027] Accordingly, two further jars were used for testing, with now an excess of acid being added to the jars to promote the conversion of dried, solid-form cellulose nanocrystals to acid-form, charged cellulose nanocrystals. Coupon **S3** was tested as a control test in a jar comprising 500 grams of water, 25 grams of sea salt and 60 grams of an acid, in this example phosphoric acid (H_3PO_4 , reagent grade), as seen in table 2. In other embodiments, other acids such as sulfuric acid can be used. This resulted in a corrosion rate for the steel (**S3**) coupon of 14.4 mpy. As expected, this corrosion rate is higher than that for coupons **S1** and **S2**, due to the well-known corrosive nature of acid.

[0028] Coupon **S4** was next tested in a jar having 500 grams of water, 25 grams of sea salt, 60 grams of phosphoric acid (reagent grade) and 34 grams of cellulose nanocrystals, as seen in Table 2. This resulted in a corrosion rate of 12.0 mpy, compared to the corrosion rate of 14.4 mpy when only salt solution and acid were present. The corrosion rate of the steel thus went down by 20 percent after adding the cellulose nanocrystals. This testing accordingly supports the conclusion that when cellulose nanocrystal fibrils are caused to be charged, they are attracted to ionic components of the corroding ferrous surface, form a coating around the ionic components of the metal surface and prevent electrochemical reactions from driving the corrosion process thereby.

[0029] The charged cellulose nanocrystals may be used as a part of a liquid composite that includes a paint formulation. The liquid composite can, for example, include: aqueous or organic solvents; miscible or emulsion mixtures of these two solvents; and gels. In this case, dried cellulose nanocrystals when dispersed within the paint formulation causes the releases of the charged cellulose nanocrystals. There are a wide variety of applications in which this composite may be used. For example, a composite comprising charged cellulose nanocrystals fibrils in a paint formulation may be used, for example, to protect: a painted steel tank, bridge, or automobile; and the painted components of an aircraft or helicopter. These applications are by way of example only, and charged cellulose nanocrystals as herein described may be used in many other applications to inhibit corrosion.

[0030] Charged cellulose nanocrystals fibrils may also be used in a variety of liquid applications not involving paint. In this case, the charged cellulose nanocrystals fibrils may be dispersed in a liquid to protect, for example: the steel structure of a power station cooling tower; a pipeline carrying hydrocarbons; and the various components of an automobile radiator automobile engine block. Here too these applications are by way of example only, and charged cellulose nanocrystals as herein described may be used in many other applications to inhibit corrosion.

[0031] Charged cellulose nanocrystals may further be used as part of a cutting fluid composite that includes cutting fluid suitable for metal cutting operations for cutting steel, brass and aluminum, for example. The cutting fluid component

may be an off-the-shelf coolant and lubricant configured for metalworking and machining processes. Cutting fluids per se are well known to those skilled in the art and their components and functionings will therefore not be described in detail. The charged cellulose nanocrystals within the fluid composite may inhibit corrosion of the metals to be cut and the cutting tools and related machinery in a manner as substantially described above.

[0032] Further testing of aluminium (A2024-T3) and brass (yellow brass) coupons was performed with acid and with acid combined with cellulose nanocrystals, with corrosion rates increasing from 77 mpy to 135 mpy, respectively for the aluminium and 0.7 mpy to 1 mpy for the brass. It appears as though a synergistic effect is occurring between the excess acid and charged cellulose nanocrystals for these metals that leads to higher corrosion rates. It is expected that corrosion rates for these non-ferrous metals would decrease in accordance with the above set out model upon performing further testing in which the excess acid is next removed after converting the cellulose nanocrystals to its charged, acid-form.

[0033] It will be understood by someone skilled in the art that many of the details provided above are by way of example only and are not intended to limit the scope of the invention which is to be determined with reference to at least the following claims.

What is claimed is:

1. A corrosion inhibitor comprising:
a plurality of charged cellulose nanocrystals fibrils.
2. The corrosion inhibitor as claimed in claim 1 wherein the cellulose nanocrystals are in acid-form.
3. The corrosion inhibitor as claimed in claim 1 for use in inhibiting corrosion in ferrous metals.
4. The corrosion inhibitor as claimed in claim 1, wherein the charged cellulose nanocrystals fibrils are attracted to ionic components of a corroding metal surface.
5. The corrosion inhibitor as claimed in claim 4, wherein the charged cellulose nanocrystals so attracted form a coating on the metal surface and inhibit electrochemical reactions from driving the corrosion process thereby.
6. The corrosion inhibitor as claimed in claim 1 wherein the cellulose nanocrystals are negatively charged and function as an anodic corrosion inhibitor.
7. The corrosion inhibitor as claimed in claim 1 wherein the cellulose nanocrystals are positively charged and function as a cathodic corrosion inhibitor.
8. The use of the inhibitor as claimed in claim 1 in a paint formulation.
9. A corrosion-inhibiting cutting fluid composite comprising:
a cutting fluid; and
the corrosion inhibitor as claimed in claim 1.
10. The cutting fluid as claimed in claim 9, wherein the charged cellulose nanocrystals fibrils are configured to be attracted to ionic components of a corroding metal surface.
11. A process for inhibiting corrosion of metal equipment where water can reside, the process including adding an effective corrosion inhibiting amount of charged cellulose nanocrystals.
12. The process as claimed in claim 11, further including dispersing the cellulose nanocrystals within the water.
13. The process as claimed in claim 11 further including causing the cellulose nanocrystals to be negatively charged, the cellulose nanocrystals so charged functioning as an anodic corrosion inhibitor.

14. The process as claimed in claim **13** including the step of causing the cellulose nanocrystals to be negatively charged via acid hydrolysis.

15. The process as claimed in claim **11** including the step of causing the cellulose nanocrystals to be in acid-form.

16. The process as claimed in claim **11** further including causing the cellulose nanocrystals to be positively charged, the cellulose nanocrystals so charged functioning as a cathodic corrosion inhibitor.

17. The process as claimed in claim **11** further including selectively causing a first set of the cellulose nanocrystals to be negatively charged, the first set of the cellulose nanocrystals so charged functioning as an anodic corrosion inhibitor, and selectively causing a second set of the cellulose nanocrystals to be positively charged, the second set of the cellulose nanocrystals so charged functioning as a cathodic corrosion inhibitor.

18. The process as claimed in claim **12** further including providing metal equipment that is ferrous.

19. The use of charged cellulose nanocrystals as a corrosion inhibitor.

20. A corrosion inhibitor consisting of a plurality of charged cellulose nanocrystals fibrils.

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