Title: METHOD FOR LIFE EXTENSION OF CELLULOSE INSULATION IN POWER TRANSFORMERS OF ELECTRICAL APPARATUS

Abstract: The present invention relates to a method for delaying the ageing, or lower the rate of degradation and loss of physical strength, of a cellulose insulation e.g. used in an apparatus such as a power transformer, an electrical apparatus or an electrical cable. The invention is achieved by that at least two ageing inhibitors in the form of active chemical substances are added to the oil in the apparatus and at least partly be absorbed by the cellulosic insulation, a first active chemical substance is a buffer substance, such as oil soluble amines- or ammonium salts, and a second active chemical substance is an oil soluble alcohol, and thereby achieving a deceleration of both the acid hydrolyses process and the oxidation process resulting in a lower rate of cellulose degradation and maintaining the strength of the cellulosic insulation.
METHOD FOR LIFE EXTENSION OF CELLULOSE INSULATION IN POWER TRANSFORMERS OR ELECTRICAL APPARATUSES

TECHNICAL FIELD

This invention relates to a method for maintenance of cellulosic insulated power apparatuses and more specifically by adding an ageing inhibitor, a "paper stabilizer package", to the oil for power transformers or electrical apparatuses with cellulosic insulation. The ageing inhibitor will thereafter be absorbed at least partly by the cellulose. The addition of such an additive could be used as a stand-alone action at any time but is preferably used together with oil reclaiming. The intended effect is to lower the rate of cellulose degradation in said apparatuses in order to maintain strength of the cellulosic insulation. The package comprises one or more different chemical compounds.

BACKGROUND OF THE INVENTION

Power transformers and other electrical apparatuses are often designed for using oil impregnated cellulose as electrical insulation and mechanical support of high voltage conductors.

Even though it takes up space and decreases theoretical efficiency, the insulating materials in a transformer is very necessary, providing both electrical separation and mechanical support for the active materials. Insulating materials must not only meet exacting electrical, chemical, mechanical and thermal requirements but must also be economical to apply. The search for better insulating materials goes on continually, however the most satisfactory practical material found to date consists of cellulose applied as Kraft paper or pressboard. Cellulose insulation is economical because of low cost raw materials fabricated in a continues high speed, low manpower process. The huge industry furnishing this material offers a reliable source
of quality product in an unending variety of grades, shapes, thicknesses, densities etc.

Cellulose used in paper manufacturing comes from vegetable fibers, mainly wood pulp, and in itself is inert chemically showing no pronounced acid or basic reaction. Cellulose in nature is combined with lignin to form woody tissue (wood pulp) in proportion of about 50 to 60% cellulose to 20 to 30% of lignin. The lignin in wood fibers must be removed by chemical reaction at the pulp mills to obtain almost pure cellulose for paper making.

Cellulose is a classic example of a polymer with an intrinsically stiff backbone. Its chain molecule is a string of condensed ring shaped glucose molecules. This long chain of cellulose gives high tensile strength and high melting point necessary for good isolating materials.

It is however well known that the ageing rate of the cellulose increases with increasing temperature, typically it doubles every 7-8 degrees Celsius.

The temperature is often limited to a maximum value during rated load and conditions. In a transformer the so-called hot-spot temperature is for normal Kraft paper limited to 98°C. The ageing rate will increase when the content of oxygen, water and organic acids in the paper increases.

In some countries the oil is stabilized against oxidation by adding an oxidation inhibitor. It is possible that this additive, at least to some degree, also retards the oxidation of the cellulose insulation.

Most of the apparatus with oil impregnated cellulosic insulation is made using conventional Kraft, non-upgraded paper. The population of electric power apparatus such as
transformers, reactors, oil cables etc has reached a high age compared to the expected design life, and the need for renewal and reinvestment rises. At the same time there is a desire to increase the possible loading of the apparatus. Actions that may reduce the ageing rate or allow for up-rating of the load limits for an apparatus will have a high value.

For transformers the most important maintenance actions are:
- Oil reclaiming focused on improving the condition of the oil.
- Drying focused on removing moisture from the paper.

In order to obtain an effect on the ageing rate of the paper, the maintenance action must remove the substances that have an effect on the ageing. For the hydrolysis, these are water and organic acids. The most harmful acids are those that are most water soluble, like formic and acetic acid.

Oil reclaiming is done by passing oil from a transformer, preferably in service, through columns and filters with Fullers earth where polar and ionic substances will be absorbed. To some degree this process also removes these substances from the cellulose insulation. The cleaning of the paper is improved at higher temperatures. After a reclaiming, the oil is usually reinhibited after treatment. A filtering and degassing step is usually included in the process.

Drying can be done either in the factory by e.g. the so-called "vapor-phase" technique, or in the field, where the so-called "hot-oil-spray" is an efficient method. In both methods the oil is tapped off the transformer tank. The "hot-oil-spray" method is often combined with a low frequency current heating of the winding. For both processes the heating will result in evaporation of both water and low-molecular acids from the cellulose, which reduces its ageing rate.
PRIOR ART

The two ageing mechanisms, oxidation and hydrolysis, is described in more detail in the paper "Ageing of oil-impregnated paper in power transformers" by L.E. Lundgaard et al. in IEEE TDEI Vol. 19, No.1, Jan 2004, pp 230-239. In particular the paper describes how the process earlier described as hydrolysis actually is an acid catalyzed hydrolysis from dissociated low molecular, hydrophilic acids.

It has long been known that urea, or non-acidic substances derived from urea, can be added to the oil and with time deposited in the cellulose to thermally upgrade the same, US 2,722,561. It is claimed that by adding 3% urea of the total weight of oil in a transformer results in a life time equal to what untreated paper would have at 98°C at 125°C. Lifetime is here the time under which tensile strength and resistance to folding would remain above a certain limiting value.

GB 866402 and GB 796603 show similar techniques, mainly focusing on oxidation as the primary ageing mechanism.

Later, methods for thermally upgrading of paper by introducing additives during the manufacturing process has been developed, NO 99249. These additives comprise melamin, trietylmelamin, trifenyelmetamin, diallylmelamin, tris-tertiary butylmelamin, N-tertiary butylmelamin, polyacrylamid, para-toluensulf onamid, biuret, succinonitril and difenylguanidin. The processing is done by adding the chemicals via a water solution or as a powder during the production of the paper.

US patent 3 102 159 with the title "Treated cellulosic material and electrical apparatus embodying the same" describes the same process, as NO 99249, for adding ageing inhibitors to the sheets during the production process of paper or pressboard to
arrive at "an improved sheet cellulosic product" like that above described. The patent describes how the improved sheets will get an increased thermal performance. In the 1960's parallel patents were filed in several countries. Thermally upgrading appears to reduce the ageing acceleration from water and acids, while it does not equally significant reduce the acceleration stemming from increased oxygen content. These methods are not relevant for transformers in service where normal Kraft paper is used.

Today's techniques for transformer maintenance focus on removal of water and in a more unspecific way acids. These techniques and practices do not address neutralization of the effect of ageing accelerators.

SUMMARY OF THE INVENTION

An important problem with restoring an aged Kraft cellulose insulation and reducing ageing is that the effect of maintenance like drying and reclaiming does not remove all ageing accelerators as they are chemically bound to the cellulose. The reduction in ageing therefore becomes limited. Chemically ageing inhibitors will directly reduce the effect of ageing accelerators by reducing the effects from their presence.

To add an internal reservoir of urea, as e.g. is suggested in American patent 2 722 561, for new transformers is not considered practical for older transformers, while replenishing the transformer with a mix of transformer oil and additives can be a part of a normal service operation.

The present invention relates to a method for adding special ageing inhibitors to the cellulose insulation of e.g. a power transformer, an electrical apparatus or an electrical cable.
The adding may preferably be done on-site when the apparatus is in service, or during or directly after a maintenance action like an oil reconditioning or reclaiming or transformer drying process.

It is a good method for non-upgraded paper and may even be used on upgraded paper. The "paper stabilizing package" can be prepared as a premix between the active chemicals and transformer oil.

A "paper stabilizing package" according to the invention may comprise one or more specified active chemical substances added to the paper via the oil phase. The additives may also be supplied to the oil as a stand-alone solution at any time during service.

The additive package may also be used together with other known additives like urea or urea derivatives.

Buffering substances like oil soluble amines- or ammonium salts can be added to decrease the hydrogen ion activity, and thus slow down the acid catalyzed hydrolyses.

Oil soluble alcohols may be added to block aldehyde groups that are exposed to both acid catalyzed dehydration and oxidative peeling. Furthermore they may act as radical scavengers, suppressing oxidation.

The "paper stabilizing package" may consist of one or more substances from each of these groups. The different substances are preferably added as a stock solution, dissolved in transformer oil. In the case where the addition is made directly after an oil reclamation process, the paper stabilizing additives could be added in the same stock solution as the oil antioxidant.
The object of the present invention is to reduce the ageing rate of the cellulose.

The object of the present invention is achieved by a method by which at least two ageing inhibitors in the form of active chemical substances are added to the oil in the apparatus and at least partly be absorbed by the cellulosic insulation, a first active chemical substance is a buffer substance, such as oil soluble amines- or ammonium salts, and a second active chemical substance is an oil soluble alcohol, and thereby achieving a deceleration of both the acid hydrolyses process and the oxidation process resulting in a lower rate of cellulose degradation and maintaining the strength of the cellulosic insulation.

One important advantage of the present invention is that it in one simple process can give an upgrading of the insulation system of old transformer units and thereby reducing the ageing rate of their insulation system and increasing their service life.

BRIEF DESCRIPTION OF THE DRAWINGS

For better understanding of the present invention, reference will be made to the below drawings/figures.

Figure 1 schematically illustrates the how the pH influences which ageing mechanism that will dominate.

Figure 2 illustrates in a diagram the expected strength behavior for kraft paper.

Figure 3 illustrates in a diagram a scattered situation for thermally upgraded paper.

Figure 4 illustrates the different possible options of treatment.

DESCRIPTION OF PREFERRED EMBODIMENT
In figure 1 is schematically illustrated that the dominating mechanism for acid hydrolysis and oxidative degradation depends on the pH value.

Kraft paper fibers contain 70-80% cellulose, 10-15% hemicellulose and 5-10% slightly modified lignin. The cellulose is the main structural element in the paper fiber and the paper strength depends on the fiber strength (cellulose DP) and the fiber bonding. In figure 2 is illustrated in a diagram the expected strength behavior for kraft paper and in figure 3 is illustrated in another diagram a more scattered situation for microcrepped thermally upgraded paper.

In a preferred embodiment the additive comprises of two different chemicals that are added to the transformer oil and thereafter diffuses into the cellulose and gets absorbed. These chemicals directly act as inhibitors of acid catalyzed hydrolysis and oxidative ageing that the cellulose molecules are exposed to. The two chemicals may preferable be used in a paper stabilizing package.

One of the buffering substances is oil soluble amine- or ammonium salts that is added to decrease the hydrogen ion activity, and thus slow down the acid catalyzed hydrolyses. Variations of this, applying urea and derivatives of urea has earlier been used, particularly before one started to upgrade the paper directly in the production process. Examples of substances that could be used are long-chain aliphatic amines and amine salts, e.g. hexadecylamine and hexadecyl-trimethylammonium salts.

The other substance is an oil soluble alcohol that is added to block aldehyde groups that are exposed to both acid catalyzed dehydration and oxidative peeling. Furthermore these will act as radical scavengers and by this also further suppress the oxidative degrading. Examples of substances that can be used
are long chained alcanols like e.g. cetylalcohol, or stearylalcohol.

The paper stabilizing package can be used on its own for a transformer where the cellulose has not been too heavily contaminated and/or aged. This can for example be diagnosed by measuring the content of humidity and low molecular acids in the oil, which is an indicator of how the condition of the solid insulation is. If the condition of the insulation system is acceptable the paper stabilizing package can be added directly. This could for example be done during an oil regeneration process, invoking only degassing and filtering of the oil. Transformer oil with dissolved inhibiting chemicals could then be mixed slowly into the treated oil from the transformer.

In case of a contaminated/aged insulation system, recognized by a high content of low molecular carboxylic acids, it is preferable to remove as much as possible of the water and contaminants from ageing of oil and paper. Several options of treatment are possible as shown in the figure 4.

By experience it is known that it is impossible to remove all ageing accelerating substances (Water and low molecular acids) and a blocking agent like in the stabilizing package will reduce their effects. The stabilizing package is most conveniently used by mixing it with oil and adding this mixture to the transformer in the last stage. For a reclaiming it would be during a last stage circulation, where the fuller earth filters are bypassed, and for hot-oil spray and vapor phase it can be mixed with the oil during a last regeneration/degassing procedure before the oil is filled back into the tank.

It is noted that while the above disclosure describes and exemplifying embodiments of the invention, there are several variations and modifications which may be made to the disclosed
solution without departing from the scope of the present invention as defined in the appended claims.

The ageing inhibiting additives are preferably added to the oil in connection with an oil reclaiming or transformer drying process, as described above, but may also be used as a stand-alone solution at any time during service. The intention is to reduce the ageing rate of the cellulose in an electrical apparatus like in e.g. a transformer. The additive package may also be used together with other known additives like urea or urea derivatives.
1. A method for delaying the ageing, or lower the rate of degradation and loss of physical strength, of a cellulosic insulation e.g. used in an apparatus such as a power transformer, an electrical apparatus or an electrical cable, characterized by,
- that at least two ageing inhibitors in the form of active chemical substances are added to the oil in the apparatus and at least partly be absorbed by the cellulosic insulation,
- a first active chemical substance is a buffer substance, such as oil soluble amines- or ammonium salts, and
- a second active chemical substance is an oil soluble alcohol, and thereby achieving a deceleration of both the acid hydrolyses process and the oxidation process resulting in a lower rate of cellulose degradation and maintaining the strength of the cellulosic insulation.

2. A method according to claim 1, characterized by,
- that the additive is integrated in a "paper stabilizer package".

3. A method according to claim 1 and/or 2, characterized by,
- that the package is combined by further chemical compounds such as long-chain aliphatic amines and amine salts, e.g. hexadecylamine and hexadecyltrimethylammonium salts.

4. A method according to any of the preceeding claims, characterized by,
- that the package is combined by further chemical compounds - preferably with a high boiling point - such as dodecanol, hexadecanol (cetyl alcohol) or octadecanol (stearyl alcohol).

5. A method according to any of the preceding claims, characterized by.
- that the adding is done on-site when the apparatus is in service.

6. A method according to any of the preceding claims, characterized by,
- that the adding is done during or directly after a maintenance action like an oil reconditioning or reclaiming or transformer drying process.

7. A method according to any of the preceding claims, characterized by,
- that the addition of the additive is used as a stand-alone action at any time.

8. A method according to any of the preceding claims, characterized by,
- that the additive is mixed with the oil during a last regeneration/degassing procedure before the oil is filled back into the tank.
Figure 1

Figure 2

Figure 3
<table>
<thead>
<tr>
<th>Process</th>
<th>On-line</th>
<th>On site</th>
<th>Efficiency to remove ageing accelerators (water and acids)</th>
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<tr>
<td>Reclaiming</td>
<td>Yes</td>
<td>Yes</td>
<td>Low to moderate depending on number of passes</td>
</tr>
<tr>
<td>Hot oil spray with low frequency heating</td>
<td>No</td>
<td>Yes</td>
<td>Good</td>
</tr>
<tr>
<td>Vapor phase</td>
<td>No</td>
<td>Unlikely</td>
<td>Very good</td>
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**Figure 4**
A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: HOLB, HOLG, HOLF

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE, DK, FI, NO classes as above

Electronic database consulted during the international search (name of database base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category*</th>
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Further documents are listed in the continuation of Box C. See patent family annex.

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Date of the actual completion of the international search 18 October 2006

Date of mailing of the international search report 20-10-2006

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International patent classification (ZPC)

**HO1B 3/20** (2006.01)
**HO1B 3/48** (2006.01)
**HO1G 4/22** (2006.01)

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Cited literature, if any, will be enclosed in paper form.
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