FULLER´S EARTH AS THE CAUSE OF OIL CORROSIVENESS AFTER THE OIL RECLAIMING PROCESS

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ABSTRACT

Oil reclaiming is of growing interest since it allows the increase of oil lifetime with low costs and minor environmental impact.
However, the overall reclaiming process should be carefully controlled in order to achieve a final high quality of the reclaimed oil.
In this work we report a case study of the reclamation of a non-corrosive oil content of a transformer that became corrosive, according to DIN 51353[1], just after reclamation, as a consequence of this oil treatment.
About 9.9 ton of insulating oil from a 60 kV distribution transformer was reclaimed by an on-line reclaiming process based on the "contact method" using about 1200 kg of Fuller´s earth, in contact with the oil, during 74 h. The oil was characterized by several physico-chemical tests, before and after the reclaiming process. The oil collected for analysis, after the reclamation process, was classified as corrosive, according to DIN 51353 standard. This result doesn´t comply with the specification of IEC 60296.[2]
Using several tests, we found that the corrosivity of the reclaimed oil was due to the type of Fuller´s earth used for the reclamation treatment. This conclusion shows that it is very important to perform the Sulfur Corrosive Test by DIN 51353 (discoloration of silver plate) before and after oil reclaiming process, in all the oil reclamations treatments, as an additional routine acceptance test for this oil treatment.

INTRODUCTION

Oil reclaiming is a technology that eliminates or reduces soluble and insoluble polar contaminants from the oil by chemical and physical processing.
This technology allows an used insulating oil to recover their physicochemical and dielectric properties, and simultaneously washes polar impurities from the transformer solid insulation with the transformer energized.[3]
In reclaiming processes currently available, the most commonly used adsorbent is "Fuller's earth".
"Fuller's earth" are natural clays with high superficial activity. These adsorbents are capable of cleaning polar impurities produced by oxidation of oils. These materials can be reused after their suitable reactivation, and so they do not generate waste.[4]
The oil reclaiming made using the "contact process" consists of stirring the used oil, in the presence of Fuller's earth, in a suitable container, for during a certain period of time.[3]

In the reclaiming process, oil tests performed in the laboratory are of particular importance.

Prior to regeneration, these tests are very important to characterize the oil, in order to study the feasibility of reclamation. If the oil characteristics indicate that the oil is suitable for reclaiming, it is very important to have its complete characterization, in order to plan the extension of reclamation, (duration of the reclamation, or number of cycles that the oil should be in contact with the Fuller´s earth).[4]

After the reclamation, the tests performed in the oil are very important to check the performance of the reclamation process by the characterization of the oil condition.
The set of tests performed before the oil reclamation is almost all the tests considered in the IEC 60422:

Table I – Set of tests performed before the oil reclamation

Breakdown Voltage - IEC 60156
Dielectric dissipation factor (DDF) at 90ºC, IEC 60247
Appearance and Colour ISO 2049 and CEI 60296 clause 6.6
Density - ISO 12185
Interfacial Tension at 25ºC - ASTM D971
Acidity - IEC 62021.1
Water content - IEC 60814 clause 2
Kinematic viscosity at 40ºC - ISO 3104
Flash Point (101,3 kPa) - ISO 2719 Procedure A
Deposits(IEC 60422)
Particles (IEC 60970)
Furfural content- IEC 61198
PCB content - IEC 61619
Inhibitor content (DBPC) - IEC 60666
Passivator Content (Irgamet 39) - IEC 60666
Potentially corrosive Sulfur- IEC 62535
Corrosive Sulfur- DIN 51353
DBDS – IEC 62697

After the reclaiming process, as the oil is "like a new oil" the set of tests performed are almost all the tests considered in IEC 60296. We also recommend to perform the dissolved gas analysis because it is important to characterize the "time zero" for a transformer after the oil reclamation:

Table II – Set of tests performed after the oil reclamation

Breakdown Voltage - IEC 60156
Dielectric dissipation factor (DDF) at 90ºC, IEC 60247
Appearance and Colour ISO 2049 and CEI 60296 clause 6.6
Density - ISO 12185
Interfacial Tension at 25ºC - ASTM D971
Acidity - IEC 62021.1
Water content - IEC 60814 clause 2
Kinematic viscosity at 40ºC - ISO 3104
Flash Point (101,3 kPa) - ISO 2719 Procedure A
Deposits (IEC 60422)
Particles (IEC 60970)
Furfural content- IEC 61198
PCB content - IEC 61619
Oxidation stability (Total Acidity, Sludge and Dielectric dissipation Factor) - IEC 61125 C
Inhibitor content (DBPC) - IEC 60666
Passivator Content (Irgamet 39) - IEC 60666
Potentially corrosive Sulfur- IEC 62535
Corrosive Sulfur- DIN 51353
DBDS – IEC 62697
Dissolved Gas Analysis – IEC 60567

During the reclaiming process, the oxidation inhibitors are adsorbed by the Fuller`s earth, or destroyed so it is recommended to replace the inhibitors after the reclaiming process. The most widely used inhibitor is the 2,6-di-tert-butyl-paracresol (DBPC).[5]

"CASE STUDY"

The oil reclamation – was performed in December 2012, in a distribution transformer with the following characteristics:

Distribution transformer

Transformer Type – Core

Cooling Mode – ONAF/ONAN

Breathing Mode – Free breathing

Insulating paper – Kraft Paper

Rated Power – 31,5 MVA

Voltage - 60 kV

Oil mass – 9900 kg

Year of Manufacturing - 1994

Oil Type – Esso Univolt 52 (uninhibited paraffinic oil)

Fig 1 – Partial view of the transformer and the reclaiming machine

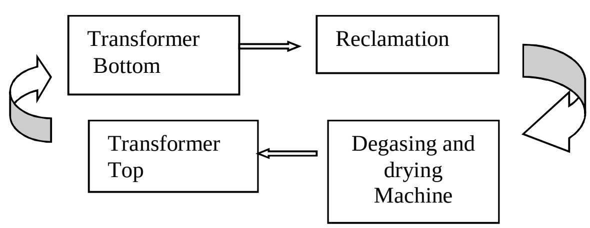
Methods and experimental conditions:

Reclamation Method – Contact Method

The transformer was maintained energized, during the reclamation process.

The reclamation system, used for this oil reclamation, besides the reclamation machine has also coupled a degassing and drying equipment.

The oil circulates continuously during 74h coming from the bottom of the transformer, flows through the two machines and enters at the top of the transformer, as shown in the following diagram:



The maximum temperature used in the different phases of the Reclaiming Treatment was 75ºC.

The Reclamation machine used for this treatment had 3 cylinders where the oil contacted with the Fuller's earth.

Fig 2 –Three cylinders where the oil is in contact with the Fuller´s earth

In each column 450 l of oil and 12,5 kg of Fuller´s earth were added, with stirring for around 20 min. After this contact time the mixture "oil+Fuller´s earth" was decanted in order to separate the Fuller´s earth with the sludge from the oil.
The Fuller's earth mixed up with the sludge was removed for future reactivation.

The oil was pumped to an auxiliary reservoir to stabilize its flow, from where was then pumped out to the degassing and drying machine, before entering in the transformer.
This circulation was repeated for more than 3 times for the total oil volume of the transformer.
At the end of the reclamation process DBPC were added to the oil, corresponding to a concentration of 0,35%.
All the results of the tests performed after the reclamation process were in agreement with the specifications contracted by the owner of the transformer and the provider of the reclamation process, except in the case of the test of Corrosive Sulfur, performed according to (DIN 51353).

Table III – Set of tests performed before and after the oil reclamation

Analysis	Before Reclamation	After Reclamation
Colour, ISO 2049	3,0	L1,5
Appearance, IEC 60296	Limpid	Limpid
Density, kg/dm^3 ISO 12185	0,8486	0,8523
Kinematic viscosity at 40ºC, mm^2/s ISO 3104	7,596	8,004
Interfacial Tension, mN/m ASTM D 971	15	30
Breakdown Voltage, kV IEC 60156	60	86
Acidity, mg_{KOH}/g_{oil} IEC 62021-1	0,17	0,03
Water content, mg_{H2O}/kg_{oil} IEC 60814	5	4
Flash Point (101,3 kPa) ,ºC ISO 2719	148,0	152,0
Deposits (IEC 60422) Sediments,%	<0,02	<0,02
Deposits (IEC 60422) Sludge,%	<0,01	<0,01
Dielectric dissipation factor (DDF) at 90ºC), IEC 60247	0,04	<0,01
Particles IEC 60970 / ISO 4406	15/13/9	17/14/10
P > 4 µm (c)	199	761
P > 6 µm(c)	56	135
P > 14 µm(c)	4	6
Inhibitor content (DBPC), % IEC 60666	<0,01	0,35
Oxidation Stability-Method C, IEC 61125 — Total Acidity, mg_{KOH}/g_{oil}	-	1,1
Oxidation Stability-Method C, IEC 61125 — Sludge,%	-	0,8
PCB's content, mg/kg IEC 61619	<2	<2
Passivator content (Irgamet 39 (TTAA)), mg/kg IEC 60666	<5	<5
DBDS content, mg/kg_{oil} IEC 62497	<5	<5
Potentially corrosive Sulfur, (NC-Non Corrosive) IEC 62535	NC	NC
Corrosive Sulfur, (NC-Non Corrosive, C-Corrosive) DIN 51353	NC	**C**
Furfural content (mg/kg_{oil}) IEC 61198		
5-HMF	<0,05	<0,05
2-AC	<0,05	<0,05
2-FAL	0,07	<0,05
2-ACF	<0,05	<0,05
5MEF	<0,05	<0,05

Fig 3 –Results of the DIN test before and after oil reclamation

It is important to underline that the result of the potentially corrosive sulfur test, done according to IEC 62535 [6], that uses a copper plate was negative in the oil sampled before and after the reclamation process. Also the DBDS content of both oil samples was less than the quantification limit, according to the results shown in Table III.

The corrosiveness of oil associated to the reclamation procedure has been already found [7] but only when high temperatures were involved in reclamation, what did not happen in this case when the highest temperature was 75ºC.

Due to the importance of this issue this analysis was repeated in prestigious laboratories from Belgium, Croatia, Slovenia, Portugal and Spain, with the same result: Positive for the DIN 51353 test.

The Belgian Laboratory has also performed the SEM-EDX analysis, as well as the analysis of the composition of the deposit found on the silver foil, after the DIN Test:

The SEM-EDX analysis revealed the presence of silver sulfide on the silver plate after DIN testing.

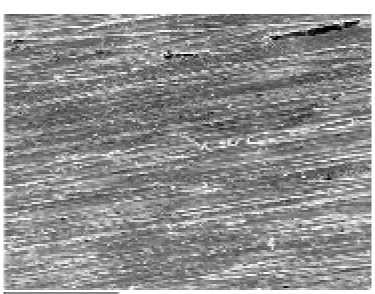


Fig. 4 – Image of the SEM-EDX Image (200 x) of deposit on the silver foil, after the DIN test

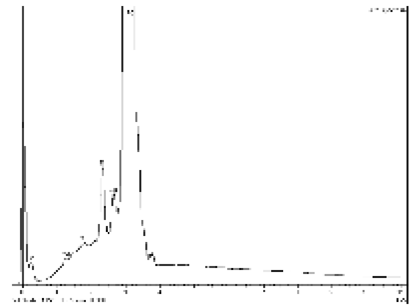


Fig. 5 – SEM-EDX Spectrum of the deposit on the silver foil, after the DIN test

In order to check which was the reason for the positive result, two Portuguese Laboratories and a Spanish Laboratory repeated the DIN test in different oils (Shell Diala D, Shell Diala DX, Esso Univolt 52 and Nynas Nytro Taurus) after having mixed up with the same type of Fuller´s earth used in this oil reclamation. The results obtained after reclamation using the DIN Test always were POSITIVE.

The referred laboratories tested those oils using a mixture of 12,5 g of Fuller´s earth with 450 ml of each oil and kept stirring the mixture for 20 min.

After this time, they decanted the Fuller´s earth of the oil and performed the DIN test 51353 and the IEC test 62535. The results of these tests are presented on Table IV.

Table IV – Results of DIN Test in reclaimed oil at laboratory scale

Oil Type	DIN 51353 Result	IEC 62535 Result
Shell Diala D	Corrosive	Non Corrosive
Shell Diala DX	Corrosive	Non Corrosive
Esso Univolt 52	Corrosive	Non Corrosive
Nynas Nytro Taurus	Corrosive	Non Corrosive

This reclamation procedure was not accepted and as the passivation with Irgamet 39, proved to be not effective, it was decided to replace the entire oil content of the transformer by new oil, in this case the oil Nynas Nytro Taurus, which is free of corrosive and potentially corrosive sulfur.

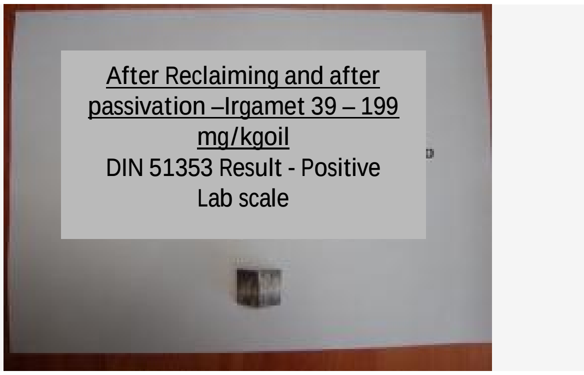


Fig 6 –Results of the DIN test after reclamation and oil passivation

CONCLUSION

As Corrosive sulfur is a very important issue, with still largely unknown consequences, all the knowledge that we can collect in order to avoid problems in the transformers in this field, is very well acknowledged.

From his paper we can draw two different conclusions:

1) It is very important to includ the Corrosive sulfur by DIN 51353 in the set of tests to be performed before and after the oil reclamation.
2) The utilities should test in advance, at a laboratory scale, the material used as absorbent in the reclamation equipment, to avoid future problems of corrosive sulfur in the transformers with reclaimed oil.

REFERENCES

[1] DIN 51353, 1985 – Detection of corrosive sulfur – Silver strip test.

[2] IEC 60296, 2012 - Fluids for Electrotechnical Applications – Unused Mineral Insulating Oils For Transformers and Switchgear.

[3] IEC 60422, 2013 - Mineral insulating oils in electrical equipment – Supervision and maintenance guidance.

[4] B.Pahlavapour; A De Pablo: W Tumiatti; M. A. Martins; M. Dahlund; G. Wilson, L. Ritchie; P. Koestinger "Insulating Oil Regeneration and Dehalogenation", CIGRE TB 413, April 2010.

[5] M. Augusta Martins, - "Regeneração de Óleos Isolantes Usados. Solução ou Problema?", Ciência & Tecnologia dos Materiais, Vol. 19, Nº 2-4 , 88-94, 2007.

[6] IEC 62535, 2008 – Insulating liquids – Test method for detection of potentially corrosive sulphur in used and unused insulating oil.

[7] Working Group A2-40 CIGRE "Copper sulphide long term mitigation and risk assessment", August 2014.