SUPERCRITICAL CO_2 CLEANING:
THE DFD SYSTEM: DENSE FLUID DEGREASING SYSTEM

G. Lumia(1) **– V. Achard**(2) **– Ch. Niemann**(1) **– Ch Bouscarle**(1) **– S. Sarrade** (1)

(1) CEA DEN/VALRHÔ, Pierrelatte – 26702, France

Email address: guy.lumia@cea.fr

(2) Société Unitech-Annemasse – ZI de Borly – 74380 Cranves Sales

Email address: unitech2@wanadoo.fr

The Supercritical Fluids and Membranes Laboratory study the supercritical carbon dioxide ($SCCO_2$) potential for cleaning working metal parts and/or machine tools. Collaborations with aeronautic, connectic… industries, allowed us to develop a specific methodology to characterise organic contaminations, with lubricants from commercial trademark (hydraulic oil, viscous lubricant, aqueous fluid…) and to define both their behaviour and their removal, from contaminated alloy parts, in $SCCO_2$.

$SCCO_2$ efficiency cleaning assessment allowed us to set a cleanliness level and to compare it with the one generally used in the cleaning industries. Several tests on a restricted number of organic contaminants applied on real elements with complex geometry and recessed holes have been performed with a 10 litre rotating autoclave lab scale prototype according to an original concept.

At the same time, a collaboration has initiated with an industrial degreasing machine manufacturer (the Unitech-Annemasse company) for a $SCCO_2$ cleaning machine engineering called DFD System: Dense Fluid Degreasing System, a CEA patented process with all innovative functions and a capacity of 100 litres. DFD System is an integrated process (with an easy to use push-button concept) for end-users with cleaning pre-selected programs.

Today, the DFD System is ready to be traded at the same price as up-market conventional machines (recycling solvent process).

I – INTRODUCTION

With the deadlines for the phase-out of ChloroFluoroCarbons (CFC's) and other ozone depleting solvents closing in, most of concerned companies are changing their current manufacturing or cleaning processing operation to accommodate new environmentally and un-hazardous acceptable solvents [1]. Cleaning by $SCCO_2$ is an alternative to conventional industrial cleaning with initial organic solvents and water-based with detergents [2].

Collaborations allowed us to develop a methodology to classify organic contaminations (hydraulic oil, viscous lubricant, corrosion protection film…) and to define their behaviour in $SCCO_2$ (solubility and unextracted fraction) expecting their removal. Tests on real factory elements with complex geometry have been performed with a new 10 l. rotating autoclave prototype [3]. Then, we have been performed tests on numerous alloys parts issued from several partners in metal working on DFD System (100 litres of capacity).

II - PARTNERS INVOLVED IN A CLEANING PROJECT

Our Laboratory was involved in a European Program with the major aeronautical industries (Airbus industry,…). The aim was the substitution of VOC (Volatil Organic Compound) in the numerous cleaning operations for aeroplane building with reduction of VOC. We have initiated new collaborations with connectic and metal working industries (Radiall…). The aim was the substitution of trichloroethylene that began prohibited against a new European legislation 1999/13 (cancer hazard, R45 classification) [4]. For the commercial scale DFD System, we have initiated a collaboration with the French major manufacturer of degreasing and washing machines: Unitech-Annemasse.

III - EQUIPMENT

Various commercially available oils (Mobil, Shell, Castrol…) were studied in laboratory bench: with a membrane pump and 1 litre extraction autoclave and two steps of 0.3 l. cyclone separators with pressure regulation. Cleaning optimisation parameters on real alloy parts were treated in a similar CO_2 loop with a 10 litre rotating cleaning autoclave developed against an original CEA patented design shown in figure 1 [3][5]. The commercial scale tests have been performed on DFD-System designed and built by Unitech-Annemasse including devices proposed by CEA: 100 litres rotating autoclave, conventional basket mainly used in screw cutting, valve pump, CO_2 distillation recycling system, automatic monitoring with tactician screen, to induce an easy to use push-button concept for End-users shown in figure 2.

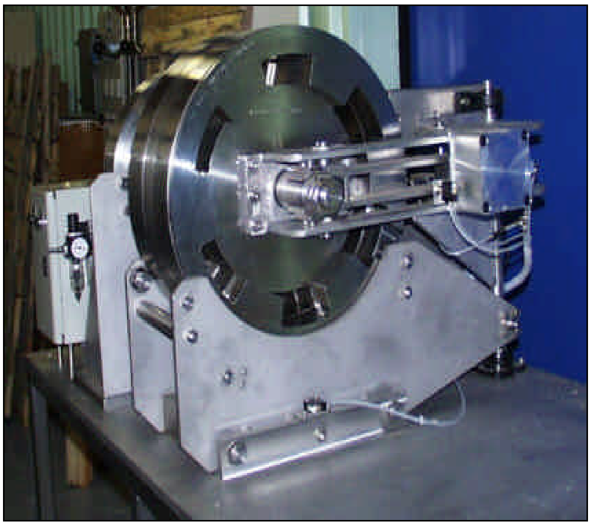


Figure 1 : CEA Prototype 10 litre rotating autoclave

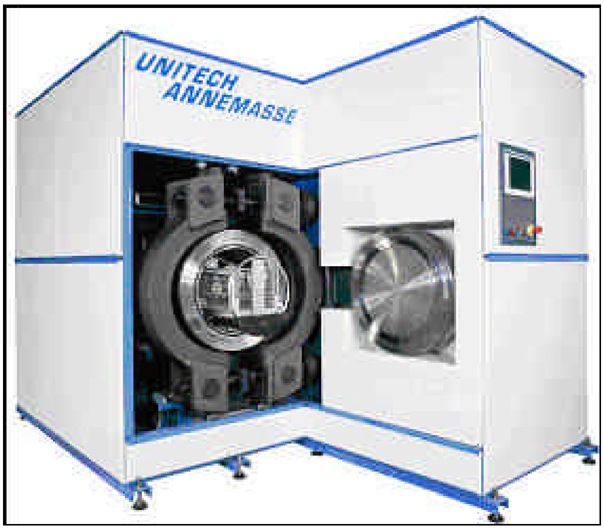


Figure 2 : DFD System : Dense Fluid Degreasing System

IV - EXPERIMENTAL PROCEDURES

IV-1 - Organic lubricants $SCCO_2$ solubility:

The solubility determination consists in an evaluation of the $SCCO_2$ mass used to extract a given lubricant mass blended with neutral solid phases (silica powder) by sampling oil extracted against chosen time steps. The CO_2 operating conditions was 20 MPa and 313 K for the following organic compounds: Viscous oil (A), Anticorrosion film (B), Hydraulic oil (C), Watersoluble mineral oil (D), Drawing oil (E), Graphite grease (F)(1). Our method consists in performing an extraction kinetic by a determination of the mass of extract product according to the necessary CO_2 mass consumed. The several partial slopes integration of the curve gives the apparent solubility rate [3].

IV-2 - Contaminated small mechanical part cleaning:

This evaluation is a bench scale experiment with real aluminium alloy small mechanical parts with complex geometry and blind holes from machine finishing, tooling and cutting metal chips contaminated. First tests have been performed with 20 parts (brass alloy) in a 10 l. rotating autoclave with agitation and metallic chips trap. Second tests have been performed on real alloy parts contaminated (≈1000 brass alloy parts) from industrial production line in a

---

(1) In agreement with the confidentiality contract with our partners isn't possible to give a commercial name of all lubricants used in this paper.

DFD System (100 l. rotating autoclave). Operating conditions are a synthesis of optimised conditions achieved in the first tests. $SCCO_2$ operating conditions were applied from 10 to 30 MPa for pressures, from 313 to 353 K for temperatures, during 10 to 30 min. For industrial evaluation, the last test consists in white paper wiping parts before and after CO_2 cleaning. Efficiency cleaning must be shown by absolute spotless white paper.

V - RESULTS AND DISCUSSION

V-1 - Organic lubricant $SCCO_2$ solubility:

The solubility seems to vary according to the chemical composition and the very low values of solubility are not a drawback for the cleaning process of metal parts.

This ratio will be used to perform several classifications in descending order according to mean apparent solubility and unextrated fraction shown in table 1.

Table 1: Classification according to the CO_2 solubility and unextracted fraction rates [3]

Contaminant	Solubility rank	Unextracted rank	Sum of both	Resultant classification	Cleaning mention
Viscous oil (A)	2	1	3	**1**	***Easy***
Hydraulic oil (C)	2	2	4	**2**	
Graphite grease (F)	1	5	6	**3**	
Anticorrosion film (B)	2	4	6	**3**	
Water soluble mineral oil (D)	5	3	8	**5**	
Drawing oil (E)	6	6	12	**6**	***Hard***
Industrial lubricant (Vacmul)	**2**	**1**	**3**	**1**	***Will be easy to clean***

In all cases, the difference of solubility ratio and unextracted fraction depends on the chemical composition of each product in agreement with the bibliography [6].

When we associate both criteria, we can note that we get in first and second place, the Viscous oil and the Hydraulic oil which will be the easiest products to clean. Afterwards, there will be the other lubricants as well as Graphite grease, Anticorrosion film, Water soluble mineral oil and Drawing oil as products with more and more difficulties to clean. For each cleaning operation, we have performed solubility test to compare the industrial lubricant and to predict the cleaning performances.

V-2 –Real brass alloy parts cleaned by $SCCO_2$ in lab scale CEA autoclave:

Several parts in brass alloy (20 parts contaminated by Vacmul oil and cutting chips) were treated in lab scale autoclave to optimise $SCCO_2$ (pressure/temperature) conditions. In second time, cosolvant, as oxygenated solvent (ethanol, isopropanol) or chlorinated solvent (dichloromethane), were used from 0,5 to 1 %. Optimised conditions and best results are shown in table 2.

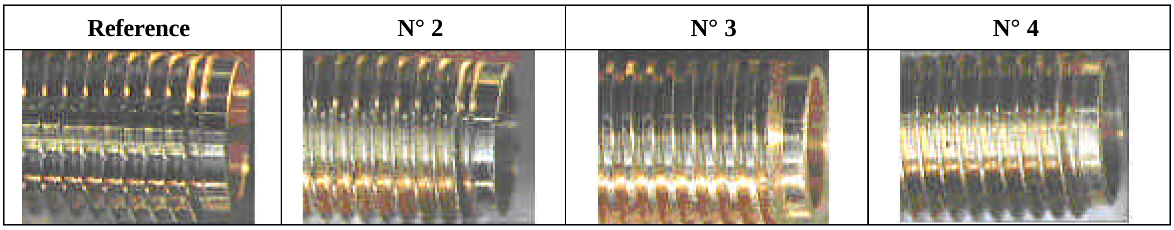
Table 2 : SC CO_2 cleaning results on brass alloy parts

Tests n°	Operating conditions					Treatment time	Observations
	pressure	temperature	flow rate	cosolvant	agitation		
1	10 MPa	313 K	100 kg/h	no	7 rpm	10 min	Light black marks, no scores, chips cutting
2	20 MPa	313 K	100 kg/h	1% ethanol	10 rpm	15 min	Light scores, no chips cutting
3	20 MPa	313 K	100 kg/h	1% isopropanol	10 rpm	15 min	Very light scores, no chips cutting
4	10 MPa	313 K	100 kg/h	1% dichloro	10 rpm	15 min	No scores, no chips cutting

All results show mild conditions of pressure and temperature. The contaminant is easy to remove according to solubility tests prediction presented in § V-1 [3].

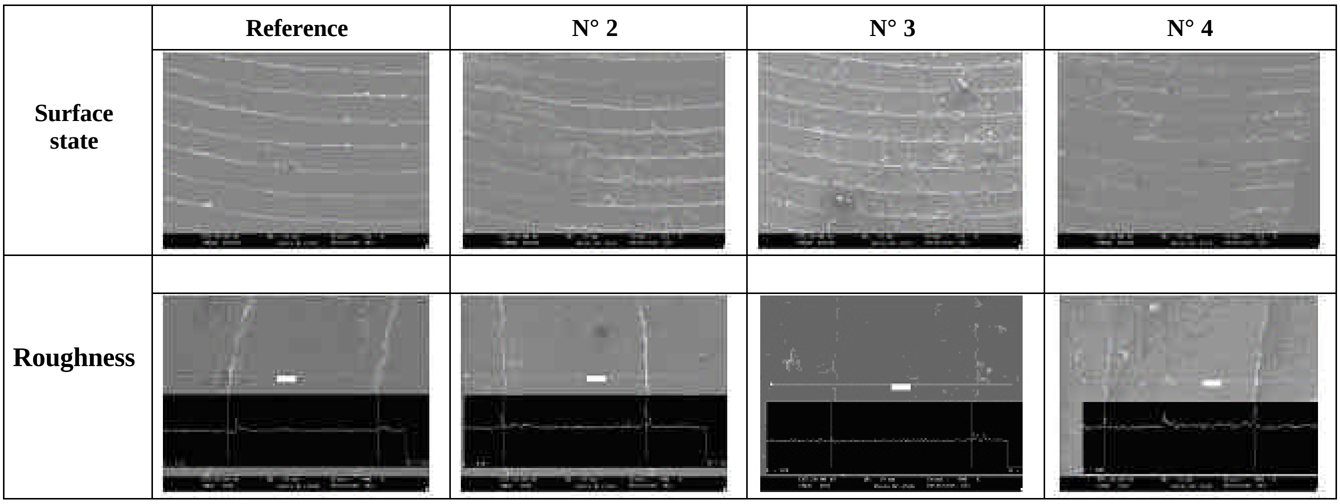
The removal of solids and lubricant by pure CO_2 was found to be increasingly unsatisfactory with very fine chips cutting (light black marks). In this case brass alloy parts seem to be very fragile and need a very mild mechanical effects (rotating speed) for preserve sparkle aspect. So, the efficient cleaning treatment must be performed with the only effect of $SCCO_2$ and cosolvant and stirring induced by mechanical effect. Efficiency were evaluated by light-optical microscopy against: Reference (parts has been dipped in trichloroethylene bath with ultrasound, 303 K, 30 minutes, as well as the actual industrial process). A comparison are performed between reference and $SCCO_2$ treated parts shown in Figure 3.

Figure 3 : SC CO_2 cleaned brass alloy parts light-optical microscopy pictures



Another tests were evaluated by SEM (Scanning Electron Micrograph) to observe surface states and roughness shown in figure 4.

Figure 4 : SC CO_2 cleaned brass alloy parts SEM pictures



From the described tests (table 2 ; figures 3 & 4), pictures show good results with $SCCO_2$ and cosolvants: ethanol, isopropanol and dichloromethane. But we can see a weak difference aspect from reference to test n° 2, 3, 4. Reference appears more sparkly and glitter than CO_2 treated parts. It seems that CO_2 cleaning remove correctly all organic compounds from the lubricant, but a very thin layer and/or inorganic elements (additives in lubricants) are not removed and which probably give a very light unpolished and dull aspect. SEM pictures confirm the first analysis with the presence of particles on the part surface especially on test n°3. Tests n°2 and 4 give a very similar results than reference. The roughness test consists in evaluating the surface integrity. These tests have given similar results from reference (background profile) to tests n° 2 and n°3 and very close with test n° 4.

V-3 –Real brass alloy parts cleaned by $SCCO_2$ in DFD System:

Several parts in brass alloy (contaminated by oil and cutting and setting chips and micro particles) were treated in commercial scale DFD System with main $SCCO_2$ (pressure/temperature) conditions: 28 MPa and 313 K. Several tests on numerous kilos of parts (≈ 7 kg: 1000 parts) were performed with pure CO_2 and cosolvants (1%) as ethanol were used from 1 to 3 % and the best tests are shown in table 3.

Table 3 : SC CO_2 cleaning results on stainless steel alloy parts

Tests n°	Operating conditions					Cleaning time	Process time	Observations
	pressure	temperature	Flow rate	cosolvant	agitation			
1	28 MPa	313 K	500 kg/h	no	10 rpm	16 min	36 min	Very small quantity of chips cutting, no scores
2	28 MPa	313 K	500 kg/h	Ethanol 1%	10 rpm	16 min	36 min	Very small quantity of chips cutting, no scores
3	28 MPa	313 K	500 kg/h	Ethanol 3%	10 rpm	14 min	30 min	No chips cutting, no scores

The removal of solids and lubricant by pure CO_2 was found as well as lab scale result with very fine residual chips cutting and un-sparkle aspect. With cosolvant, results are acceptable by industrial without chips and marks. The process involved consist to a pressurisation during 8 - 10 minutes, a real cleaning time during 14 to 16 minutes using from 120 to 140 kg of CO_2 by re-circulation, the depressurisation last 5 minutes from the work pressure to 5 MPa (isobar with the distillation module) and toward events during 5 minutes more (90 % of CO_2 is recycled for each cleaning operation). The global process needs only 30 to 36 minutes for this parts according to an industrial rate.

A comparison are performed between reference and $SCCO_2$ treated parts on white paper test shown in figure 5.

Figure 5 : SC CO_2 cleaned stainless steel alloy parts on white paper tests pictures

Un cleaned part	Reference	Test n° 1	Test n° 2	Test n° 3
				

The pictures show a similar aspect between reference and tests n°1 to n°3. The most close is the test n°3 with a sparkle aspect and without chips and black marks on white paper.

V - CONCLUSION

First of all, the methodology based on the solubility and the unextrated fraction has shown interesting results, useful to determine the lubricant behaviour in $SCCO_2$ and the cleaning ability.

According to Dahmen *et al.*, pure CO_2 (and/or CO_2 and cosolvant) is an already suitable solvent for a variety of cleaning applications [7]. Several tests performed on lab and commercial scale show interesting results with a good cleaning efficiency, close to reference cleaned parts. Nevertheless, a very thin layer film remains on the part surface from CO_2 unextracted lubricant fraction. The achieved cleanliness level must be acceptable against applications for intermediate cleaning (inter-operations) or classical cleanliness level. For a high level, oxygenated solvent (environment friendly and un-hazardous), additive effects must be usable as ultrasound (in process on DFD System) and CO_2 blasting. DFD System is already to be used by industrial companies with a correct cleaning quality, with an acceptable rate, with a reasonable cost-performance ratio (close to up-market degreasing machine) and a solution of substitution of conventional inflammable or chlorinated organic solvents with a low waste volume.

ACKNOWLEDGEMENTS:

This communication is based upon work funded by the Agence de l'Eau Seine-Normandie via the SATS (Syndicat national des entreprises d'Applications et de revêtements et Traitement de Surfaces).

Radiall Company is gratefully acknowledge for having provided the real alloy parts and expertise on CO_2 cleaned material.

The authors want to thanks ANVAR Rhône-Alpes (Agence Nationale de la Valorisation de la Recherche) for the loan to the DFD System setting.

REFERENCES:

[1] KABYEMELA, B., M., KANNO, A., KANNO, M., SMITH JR. R., L., INOMATA H., ARAI K., Proceeding 5th International Symposium on Supercritical Fluids, Atlanta, USA, **2000**.

[2] DAHMEN, N., SCHÖN, J., DINJUS, E., Proceeding 5th International Symposium on Supercritical Fluids, Atlanta, USA, **2000**.

[3] LUMIA, G., BASSAN, S., PERRE, Ch., SARRADE, S., Proceeding 7th Meeting on Supercritical Fluids, Tome 1, Antibes, France, **2000**, p. 375

[4] Directive 1999/13/CE du Conseil du 11/03/99 – JO n°2085, France, 29/03/**1999**, p. 1

[5] LUMIA, G., PERRE Ch., BASSAN, S., Patent n°: PCT/FR/**00**/13453. Process, device of contaminated parts cleaning by pressurised dense fluid.

[6] DAHMEN, N., SCHMIEDER, H., SCHÖN, J., WILDE, H., High pressure chemical Engineering, PH., RUDOLF VON ROHR & CH. TREPP (Editors) Elsevier Science B., V., Forschungszentrum Karlsruhe, Institut für Technische Chemie CPV, Karlsruhe, Germany, **1996**, p.515

[7] DAHMEN, N., SCHÖN, , J., DINJUS, E., Precision cleaning using compressed carbon dioxide., Proceeding 7th Meeting on Supercritical Fluids, Tome 1, Antibes, France, **2000**, p. 369