Cleaning and surface treatment

SEPAREX developed a process for cleaning parts using liquid carbon dioxide (precision cleaning), with the aim of substituting the harmful chlorinated solvents by the environment-friendly CO_2 . Several equipments were built and tested, one sold to a high-tech client for surface treatment before sticking glass window on an aluminum alloy (optoelectronics). However, several issues are refraining potential customers: low solvent power of the fluid, absence of an efficient package of surfactants to boost cleaning efficacy, high price and long cleaning cycle in comparison with the classical processes.

At present time, significant efforts are dedicated to wafers processing by the micro-electronic industry in order to deal with the technological gap related to the introduction of extremely high-density grafting on silicon wafers. SEPAREX contributes to this effort by supplying its know-how, especially on equipment design and construction to two European consortiums. Two prototype systems for cleaning and surface processing (photoresist removal) are being built.

NATURAL AND FORCED CONVECTION IN PRECISION CLEANING AUTOCLAVES

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Abstract
Chloroalkanes substitution by liquid carbon dioxide for precision cleaning is a major environmental challenge that requires innovative solutions to reach both high quality cleaning and acceptable costs. One technical problem consists in causing a strong convection inside the cleaning autoclave in order to boost mass transfer of pollutants to the fluid and to entrain particles. Several techniques have been proposed : Forced convection through a motor-driven blade stirrer, ultrasonic agitation, free connection. In this paper, a special autoclave design is disclosed, permitting both forced and free convection of the liquid carbon dioxide and experimental results are presented to show convection efficiency on cleaning.

Introduction
Despite implementation and cost constraints of high pressure equipments, carbon dioxide is becoming one of the most attractive substitute to chlorinated and CFC solvents and one of the most promising solvents to the always more demanding precision cleaning industry, especially for complex parts with very thin holes or grooves. In fact, besides its low toxicity and environmental effects, CO_2 has exceptional properties of diffusion, which may be deciding for the completion of better cleaning results.

That is why carbon dioxide is now competing with halogenated solvents - which are under new implementation constraints because of their health and environmental hazards -, other non-hazardous solvents (hydrocarbons, perfluorinated hydrocarbons or ethers, …) and aqueous systems for both textile dry cleaning and industrial parts degreasing.

Many patents and articles are now appearing, mainly in the USA where a very significant effort is made to substitute perchlorethylene for dry cleaning and trichlorethylene for precision cleaning by liquid CO_2. However, the industrial development of processes using CO_2 requires :

- Optimized cleaning cycles minimizing residence time of the items in the cleaning zone ;
- Adequate surfactants for a high quality cleaning with minimized CO_2 and energy consumptions [1-3] ;
- Fully automated cleaning machines which have to be easily operated and maintained by non-specialists.

SEPAREX has developed a cleaning machine [4] adapted to treatment of mechanical or electronical parts made of metals, polymers, composites, … using liquid CO_2 as solvent : it is fully automated for an easy operation, including fast closure of the autoclave. Carbon dioxide is not recycled, and it can be added a surfactant and/or a co-solvent. The volume of the cleaning autoclave is 60 liters.

Process and machine description

As the plant is intended to be operated in mechanical or electronical shops, operation and maintenance have to be very easy and require as least time as possible. It is the reason why we choose to simplify the process :

- No CO_2 recirculation, what means that no CO_2 pump is necessary ;
- No heating/cooling medium circulation.

This leads to the general flow sheet presented on figure 1 :

Liquid CO_2 from the storage (10 to 20°C, 50 bar) is introduced in the cleaning autoclave (1), possibly added with a co-solvent or a surfactant through a small pump (2). In the cleaning autoclave (1), a basket (3) is designed to receive the parts to be cleaned : the liquid CO_2 is subjected to natural convection induced by a gas-lift, as described later, and/or to forced convection induced by a turbine (4) moved by a variable-speed motor (5) through a magnetic driver. The cleaning autoclave closure system is fully automated (Cf. picture 1) and the basket can be moved in and out by a hoist. CO_2 exits the autoclave through the bottom and is further reheated in the electrically-heated exchanger (6) prior to oil separation in a high performance cyclonic separator (7). CO_2 flow rate is controlled by an automated needle valve (8) under control of a mass flow meter (9). In order to avoid a low temperature exploration that might destroy or heavily damage the parts, nitrogen or dry air is introduced in the autoclave at the end of the cleaning cycle, prior to final CO_2 venting.

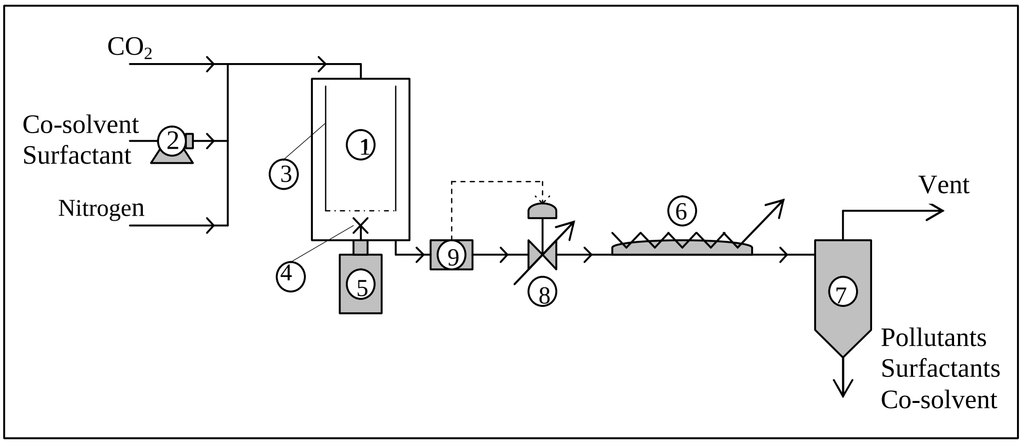
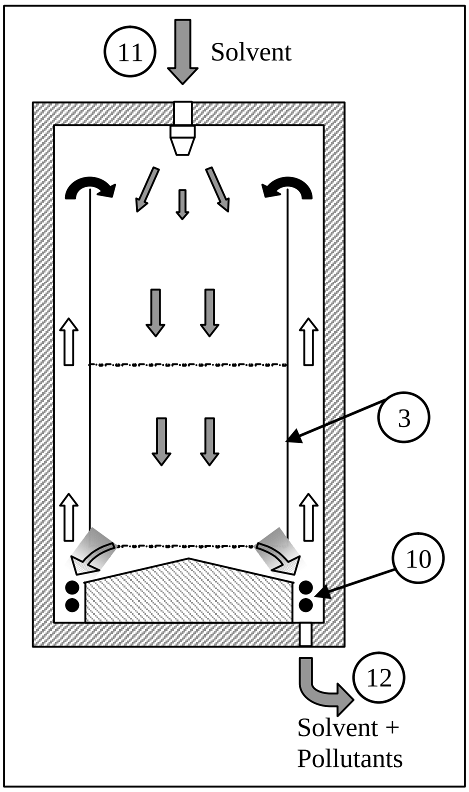


Figure 1. General flowsheet

High reliability and safety are obtained by failsafe systems as common practice in CO_2 extraction plants. The cleaning cycle and all process operations are managed by a computer, including safety functions.

In fact, the main originality consists in the autoclave design that is described in a recent patent application [4] : according to the schematic view presented on figure 2, the basket (3) containing the parts to be cleaned is a cylinder, closed at the bottom by a metal grid, of a diameter slightly lower than the internal autoclave diameter so as to maintain a cylindrical annular passage for the fluid ; the bottom of the autoclave is designed with an open annular channel in which is set an electrical resist (10). At the beginning of the cleaning procedure, liquid CO_2 is introduced from a nozzle or a distributor (11) fixed on the autoclave lid and fill the autoclave until it reaches a level N, just below the basket upper section. At that moment, the resist (10) is turned on : the heat provokes a partial vaporization of CO_2 in contact with the resist, what induces a gas-lift convection through the passage between the basket and the autoclave walls. The two-phase fluid mixes with the colder “fresh” CO_2 arriving through (11) and condenses to a liquid phase that falls again onto the pieces. During this cleaning time, a small flow rate of CO_2 is added through (11) meanwhile a similar amount of fluid is withdrawn at the bottom port (12) in order to maintain a quasi-constant quantity of CO_2 inside the autoclave. It is to be noticed that most pollutants dissolved in CO_2 while leaching the parts are precipitated onto the resist as CO_2 density is decreased and are carried away with the exiting fluid prior to their further recovery in separator (7) - (cf. figure 1).



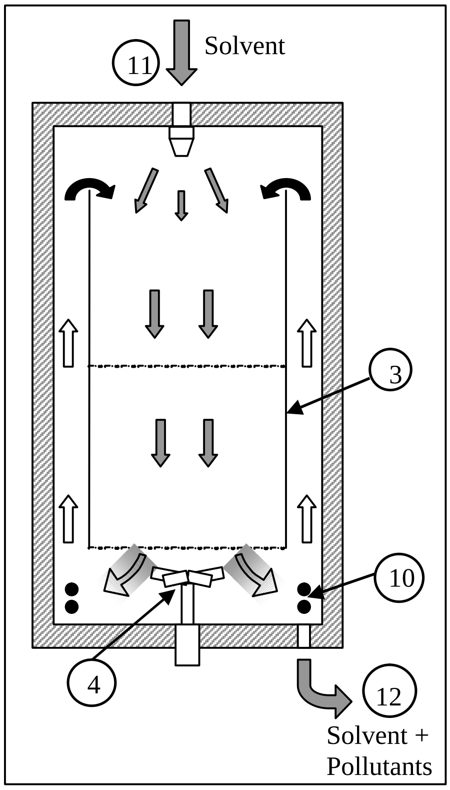


Figure 2 : Natural convection

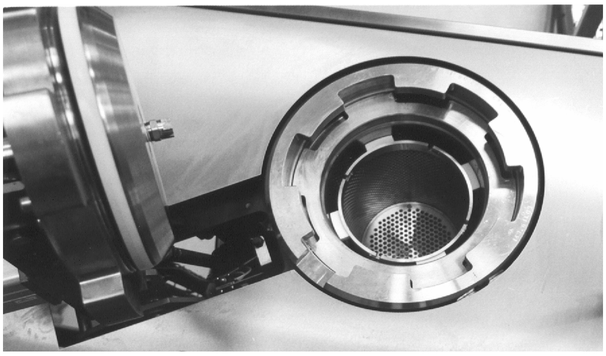
Figure 3 : Forced convection

Experiment

In order to evaluate the efficiency of the natural (gas-lift) and forced convection on cleaning, a wide experimental plan was realized, using very difficult conditions in order to evaluate the impact of the various parameters. In fact, parts are covered with a quantity of oil far more important than commonly found in mechanical shops : by this way, these “hardest conditions” allow to compare the results so as to evaluate the cleaning efficiency observed during the different runs, while this would have been impossible with “real” oil contamination amounts.

<u>Materials</u>

All experiments are made with the same metal parts, chosen as complex nuts, tees and connections currently used in plumbing, made of cast iron, carbon steel, stainless steel and brass (see picture 2). At first, they are immerged in the selected oil and then collected in the basket in which they are cleaned with liquid CO_2.
CO_2 is European Standard Quality from CARBOXYQUE.



Picture 1. Cleaning Autoclave (60 liter)

Picture 2 : Parts to be cleaned

Two contaminants are used :

- A soluble machine oil : TEXSOL H3 from Texaco mixed with water (5% oil) taken after use on a lathe.
- An engine oil : CARTER 220 from Elf.

Measurements

After cleaning with liquid CO_2, the pieces are subjected to a very intense cleaning in an ultrasonic bath using chloroform ($CHCl_3$) as solvent ; the resulting solution is carefully evaporated in a rotating evaporator and the liquid residue is weighed (± 0.1 g).

CO_2 Cleaning Cycle

- CO_2 filling (45 kg) — 4 min
- Cleaning (3 different processes) — 0 to 60 min
- Slow emptying — 15 min
- Nitrogen sweeping — 10 min

CO_2 Cleaning Processes

- Process 1 : soaking the pieces in the autoclave.
- Process 2 : soaking (1/3 of cleaning time) then emptying and rinsing with a new complete filling of CO_2 (45 kg).
- Process 3 : circulation of CO_2 through the autoclave. The amount of added CO_2 is the same as for Process 2 (45 kg).

CO_2 Cleaning Methods

These methods are efficient during the whole cleaning cycle :

- no agitation.
- natural convection (figure 2).
- forced convection (figure 3).

Results

Efficiency of the different processes and methods

Figures 4 and 5 compare the processes and methods of cleaning for the machine oil and the motor oil, with a cleaning time of 40 minutes.

Concerning the cleaning processes, the most important differences are reported for the machine oil removal with natural convection, where processes 2 and 3 reduce the amount of remaining oil by half. But almost no changes are noticed in the other cases.
The impact of the different cleaning methods is more important. Natural and forced convections improve very significantly the elimination of the two oils ; and they have the same efficiency to remove the machine oil in process 2 or 3.
But the differences between these two methods for engine oil cleaning demonstrates that the shear forces induced to remove oil from the surface of the parts are more important for the forced convection than for natural convection.

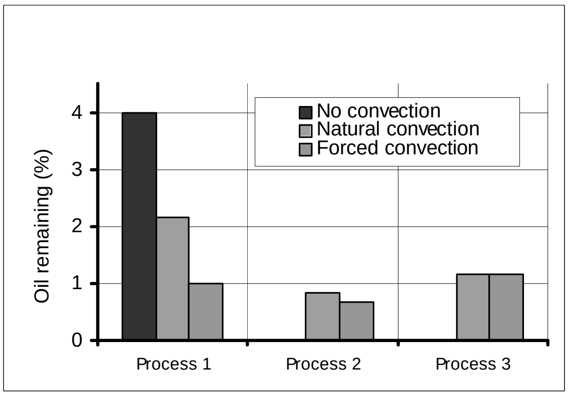


Figure 4 : Machine oil cleaning (60g)

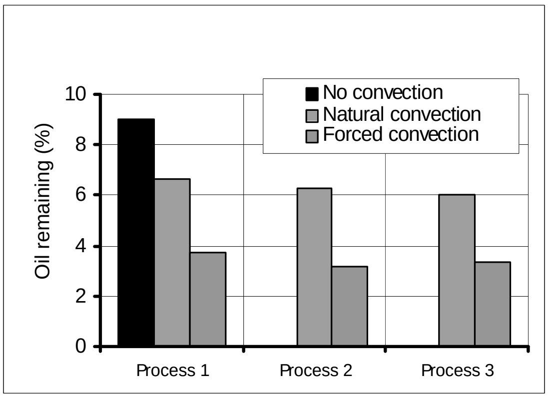


Figure 5 : Engine oil cleaning (200 g)

Influence of the amount of oil to eliminate

A known quantity of engine oil is poured on the parts to be cleaned. The cleaning parameters are as follows : process 1, natural convection, 40 minutes cleaning time. The results are presented on figure 6. They suggest that the same amount of oil remains on the pieces as far as the quantity put before is sufficient to cover completely the surface of the parts. This means that this cleaning technique leaves a layer of oil with the same thickness whatever the quantity of oil may be before.

This confirms the results shown on figure 5, the amount of oil remaining depends on the mechanical energy for cleaning but not on the oil / CO_2 ratio.

Influence of cleaning time

60 g of machine oil or 25 g of engine oil are poured on the parts to be cleaned. The cleaning parameters are as follows : process 1, natural convection, 0 to 60 minutes cleaning time. The results submitted on figure 7 show a great difference between the two oils : the maximum cleaning efficiency for the process is reached only by filling and emptying for machine oil while 30 to 40 minutes cleaning are needed for engine oil.

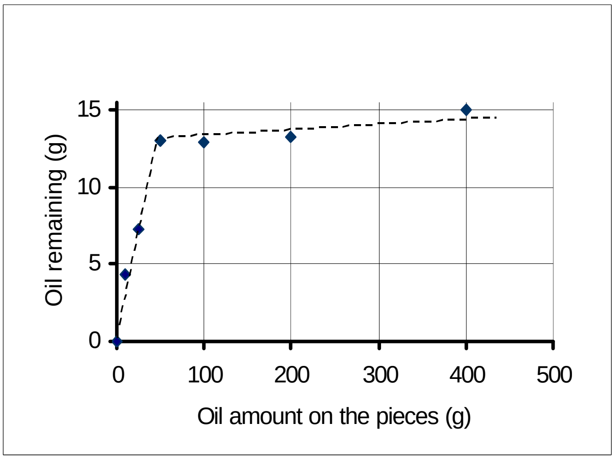


Figure 6 : Engine oil cleaning : influence of oil amount on the pieces

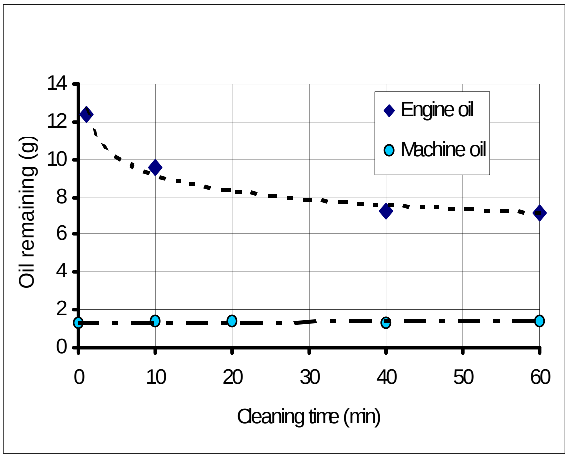


Figure 7 : Influence of the cleaning time

Surfactants

Some potential surfactants are tested to improve the cleaning efficiency of the machine. The selected conditions are as follows : process 2 (in order to rinse the parts), forced convection and 40 minutes cleaning. The pollutant is a mixture 50:50 of the two oils (50 g). About 50 g of surfactant (concentration in CO_2 : 0.1%) is added during filling in the autoclave.

The following surfactants are tested :

- Fomblin Z-DOL (Ausimont SpA) : hydroxy-terminated perfluoroalkylpolyether (Mn = 530 dalton) ;
- Q2-5211 (Dow Corning) : glycol-silicone copolymer used as superwetting agent ;
- FS1265 (Dow Corning) : fluorosilicone ;
- Tegopren 5878 (Goldschmidt AG) : polyether siloxane ;
- KRYTOX FSL (DuPont de Nemours) : carboxy-terminated perfluoroalkylpolyether (Mn = 2500 dalton) ;
- Citral : from lemon oil.

No surfactant improves the quality of cleaning (the amount of residues is always higher than without surfactant). This means that other types of surfactant must be found to improve the cleaning process. Another study of the behavior of such products should be necessary by observation in a sapphire cell.

Industrial development

Presently, SEPAREX is working on its pilot plant on various types of parts mainly originated from high-tech applications including instrumentation, opto-electronics, guidance systems, electronic boards, television parts, ...

Cleaning is efficient and most organic compounds are removed ; however, as found in the results presented here, the cleaning efficiency is often lower than the efficiency observed with chlorinated solvents :

- A thin film of oil may remain at the surface, that is not always an issue … and is sometimes wanted to avoid oxidation during the part storage ;
- Some stains of additives may appear, depending on the oil/grease composition, what suggests the need for addition of a surfactant active in liquid CO_2, to be selected case-by-case.

Finally, this study demonstrates that a very simple and inexpensive system leads to attractive results, especially when natural convection is efficient enough, what avoids any mechanical agitation.
Ultrasonic cleaning will be the next development, which may probably be beneficial to this natural convection system without complexifying the equipment.

References

[1] Micell Technologies, Raleigh (North Carolina-USA), Technical note, 1997.
[2] University of Texas/Air Products and Chemicals, Patent EP 0 814 112, 29/12/97, Priority : US 667, 132, 20/06/96.
[3] Unilever, Patent WO 96/27704, 12/09/96, Priority 06/03/95.
[4] Perrut, M., Perrut, V. ; French Patent 98.03451, 20/03/98.

7.2 Polymer processing

The unique ability of supercritical fluids to swell and plasticize polymers is crucial to many processes, including impregnation and dyeing, purification, foaming and chemical modification (grafting). Due to the extremely high economic importance of polymer processing, from polymer synthesis to polymer recycle, many books, articles and patents have been dedicated to polymer processing with supercritical fluids. I will strongly recommend to refer to a recent excellent review by Kazarian [1], meanwhile the book of Mc Hugh and Krukonis [2] remains a basic source.
Regarding specific interactions of SCF with most commercial polymers, systematic studies were recently published by Los Alamos researchers [3,4].
Many other articles are available in the Proceedings of the recent symposia.

References

[1] Kazarian S.G., Polymer processing with Supercritical Fluids, *Polymer Science*, Ser. C, **42**, 2000, p. 78-101
[2] Mc Hugh M., Krukonis V.J., *Supercritical Fluid Extraction*, Butterworths-Heinemann, 2nd edition, 1992, p. 189-292
[3] Sawan S.P., Shieh Y.-T., Su J.-H., Evaluation of the interactions between supercritical carbon dioxide and polymeric materials, *Los Alamos report* LA-U-94-2341.
[4] Spall W.D., Laintz K.E., A survey of the use of carbon dioxide as a cleaning solvent, *Los Alamos report* LA-U-95-1445 (1018).