UNIVERSITY OF PADOVA

DEPARTMENT OF INDUSTRIAL ENGINEERING

DEGREE COURSE IN ENVIRONMENTAL ENGINEERING

Inertization's Project of reactors processing flammable volatile organic liquids

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SUMMARY

Chapter 1 Introduction and goal of the thesis

1.1 Preface

The use of gas, flammable vapors and combustible dust within industrial cycles has precise technical reasons linked to production needs. Moreover, many production cycles generate hazardous solid, liquid and gaseous final wastes and/or as intermediate products treated in the same facilities.

The presence of these hazardous substances in industrial processes is associated with at least three different scenarios of accidents that can affect the safety and health of workers:

- Fire
- Explosion
- Toxic releases.

The dominance of one type of accident with respect to another is a function of both the production cycle and the quantity of the substances involved. The chemical industry process may be subject to three types of accident in the manner indicated in the Tab. 1.1.

Tab. 1.1*: Major accidents in a chemical industry.*

Incident type	Probability of occurrence	Loss related to worker safety	Potential economic loss
Fire	High	Low	Medium
Explosion	Medium	Medium	High
Toxic release	Low	High	Low

Prevention and protection measures must be implemented by the employer in order to minimize the level of risk and protect the health of workers and the environment. The scope of these strategies is the production department of the company Huber Italy, a leading global manufacturer of inks for printing. nitrocellulose and volatile organic solvents used for their production, are the critical factors that determine the properties of the extremely flammable mixture.

The strategies aiming to prevent the formation of potential ATEX (ATmospheres EXplosibles) consist of technical solutions, among which fall within the three scenarios examined in this thesis that, for reasons of simplicity, will be called A, B and C:

Scenario A or current. localized suction system of volatile gas and powdery generated in process reactors from the production and refining of flammable liquids (inks); *Chapter 3* contains a description of this system.

Scenario B. Proposal of installation of a new air extraction system that conveys the filtered air to a concentration unit, which allows to obtain polluted air with a high concentration of solvent.

Scenario C. Inerting of production reactors with inert gas in order to eliminate the explosive atmosphere; this strategy is the 'subject of study and evaluation of this elaboration. Inerting is the main strategy to prevent the formation of explosive mixtures inside the containment process. While the solutions A and B in terms of safety and risk are equal, it is proposed to assess the feasibility and improvement that the solution C can bring to the workplace in terms of risk, environmental, economic and energy.

1.1 Thesis's purpose

Safety risk at the workplace is an issue which employers and engineers must take the responsibility. Hence they must do their utmost to analyze and manage such risks, possibly preventing them.
In light of the importance of such aspects, I wanted to investigate the aspects related to the risk of fire and explosion in industrial activities. To face a real case, I've done my thesis work at a facility of the company Huber Italy, in Vicenza, where I spent 7 months. Because of the massive use of organic solvents in the production cycle, the risks of fire and explosion can not be excluded. Indeed they may represent a real risk, so my thesis is mainly focused on the issue of safety in the workplace in order to possibly improve the current situation. To deal with the current problem of fire risk, I analyzed different alternative preventive measures which are suited to the current situation. This led me to identify three different scenarios.
The thesis work has been focused on the comparison of the three different operational scenarios, including the one currently used by the company.

To analyze the risk profile, I used the software CPWin by BMSistemi to calculate the fire risk in order to numerically quantify the residual risk to which the spans of the plant of the company are currently subjected.
I performed the same procedure for the remaining scenarios demonstrating then, numerically, which is most advantageous to reduce the fire risk.
The method of analysis used in this thesis has allowed to classify the different scenarios and identify the most appropriate to prevent the risk of fire or explosion in the company.

In order to achieve an economical evaluation of the three scenarios I've evaluated the consumption of electricity, natural gas, and the maintenance costs, and the cost for the revamping of the existing plant. I considered also the environmental aspects related to the emissions to the atmosphere from the thermal oxidizer, as well as the large consumption of electricity and natural gas resulting from the operation of the post-combustor.
These three criteria - safety, economics and environment - used in my analysis are the most significant and decisive as they represent, respectively, the priority aspects of company's development.

Chapter 2 The Explosion Risk

2.1 Introduction

The explosion is a violent chemical oxidation reaction in which it generates the combustion of a substance, called a fuel, in the presence of an oxidising agent. The phenomenon is accompanied by a rapid increase of temperature and pressure and by the presence of flames. Supersonic explosions created by high explosives are known as detonations and travel via supersonic shock waves. Subsonic explosions are created by low explosives through a slower burning process known as deflagration (Fig. 2.1.1).

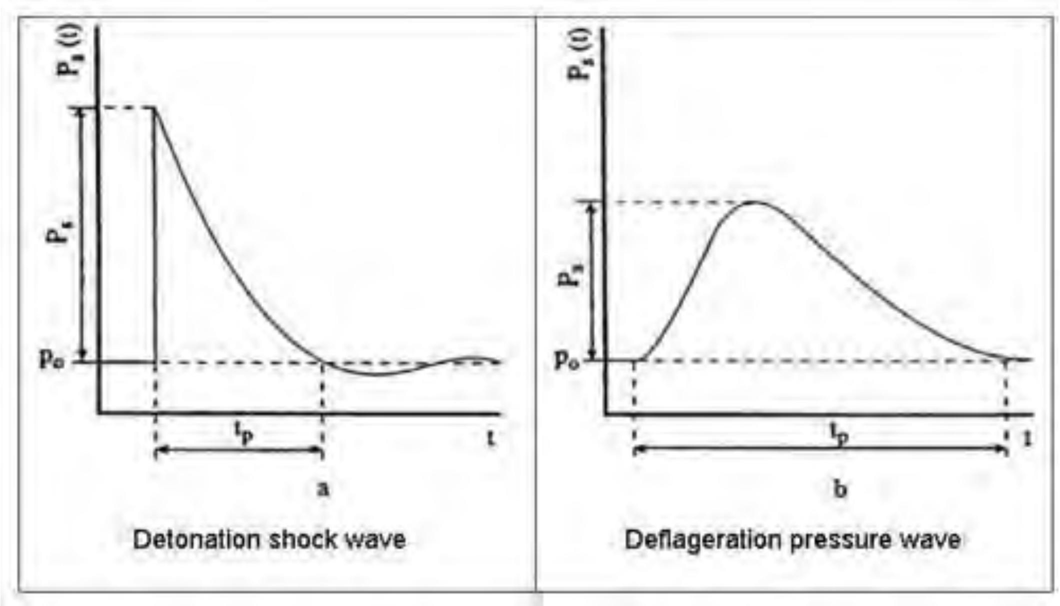


Fig. 2.1.1 : *Deflagration and detonation*.

However, it is appropriate to differentiate the phenomenon of the explosion from that of fire: the fire is a combustion that is spread in an uncontrolled way in time and in space, while the explosion combustion propagation is a very rapid with violent release of energy and it can take place only in the presence of dust or gas fumes. In order for an explosion to occur, the explosive atmosphere (ATEX) must be in the presence of a source of ignition effective, that is capable of triggering the reaction. This is represented graphically by the FIRE triangle (Figure 2.1.2), where the sides of the same indicate the three necessary conditions so that we can verify the explosive reaction. The ignition source must be able to provide the explosive mixture, for a given concentration of the substance in the air, an amount of energy sufficient for the combustion exceeds that critical point beyond which it is capable of self-sustaining, allowing the front of flame to propagate itself without supplying energy: energy that is specific to each substance and the minimum value is called the minimum ignition energy.

Fig. 2.1.2: *Explosion triangle.*

Many may be the consequences of an explosion to occur in a workplace and it is customary to differentiate injury scenarios depending on whether they originate from releases of gas, vapor, mist, spray or by combustible dusts, which have characteristics of explosion very different, despite the presence of similar properties in terms of parameters of ignition and combustion. All substances originate from an accidental release in fact present:

- Fields of explodibility sufficiently defined (LEL, UEL);
- Burning rate;
- The relationship between turbulence and combustion rate laminar;
- Phenomenon of transition from deflagration and detonation;
- Ratio of increase of pressure in case of explosion isochoric;
- Ratio of increase in volume in case of explosion isobar;
- Minimum ignition energy;
- Ignition temperature for given test condition.

Regardless of the differences in behavior that the various types of substances present, as part of the analysis of industrial explosions is customary to carry out a characterization of dangerous substances through quantitative parameters that allow to classify every aspect related to the stability from or reactivity of the substance analyzed. Following is a summary of the main parameters used to quantify the risk of explosion in substances / mixtures to the state of liquid, vapor, mist, spray or combustible dust.

2.2 Fundamental physical parameters

2.2.1 Explosion limits

The explosion limits represent the boundaries of the explosion range in which the concentration of the flammable substance in the air can lead to an explosion (deflagration or detonation). The Lower Explosion Limit (LEL) and Upper Explosion Limit (UEL) are defined as follows:

- LEL concentration of flammable substance in air below which the atmosphere does not explode;
- UEL: concentration of a flammable substance in air above which the atmosphere does not explode.

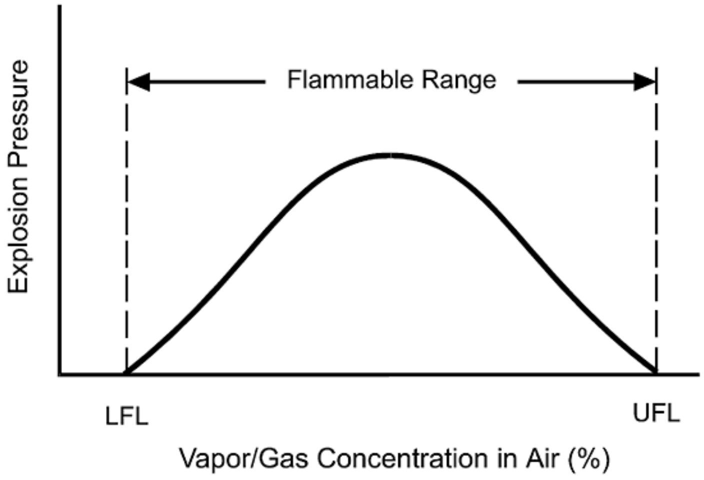


Fig. 2.2.1.1 : *Flammability limits.*

The explosion limits are measured in mixture with air (Fig. 2.2.1.1). These limits, in the case of gas, vapor or mist, they change to changing boundary conditions in which they are measured. In particular:

- Increasing the concentration of oxygen greatly expands the UEL, and therefore the field of explosion, while it has little influence on the LEL;
- An increase in temperature tends to increase the field of explosion with an increase UEL;
- An increase decided the explosion range is recorded instead with the increase in pressure which causes a strong displacement UEL (Fig. 2.2.1.2).

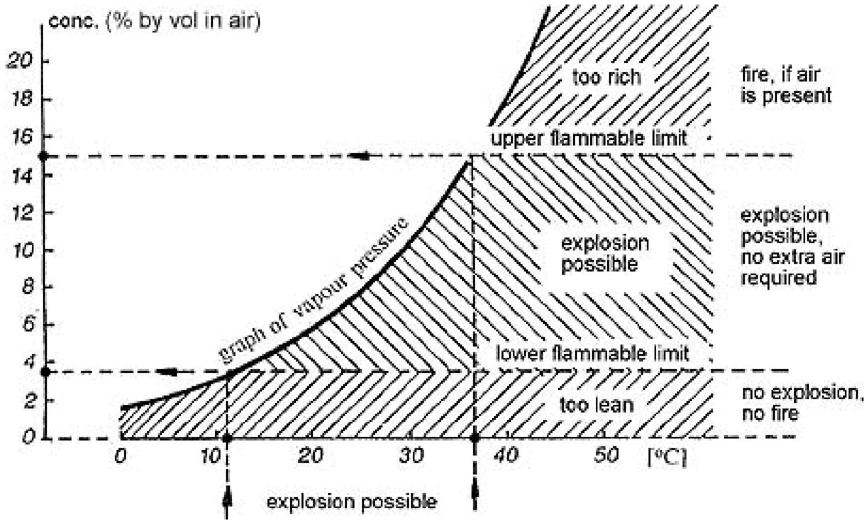


Fig. 2.2.1.2 : *Flammability temperature and pressure dependence.*

The LEL (for gases / vapors) is generally used for the sizing of the control systems of explosion while the UEL (for gases / vapors) is useful if one wants to avoid the explosion range using the strategy of saturation of the vapors in tanks of stoccagiio of flammable. The LEL of dust may be useful to determine the presence or absence dell'ATEX flows in pneumatic transport.

2.2.2 Limiting oxygen concentration

The limiting oxygen concentration (LOC) is the maximum oxygen concentration (determined in the test conditions specified) in a mixture of a flammable substance and air and an inert gas at which no explosion occurs. Below the LOC mixture is not able to generate a reaction that is self sustain and propagate the entire unburned mixture. The LOC depends both on the type of substance tested both by gas used for generating inert atmosphere. The technical standards of reference for the execution of the test are the ASTM E2079 for gases and vapors and EN 14034-4 for combustible dust. The determination of this parameter is used as the basis of prevention operations dell'ATEX defined inerting, under study. In the case of hydrocarbons it is possible a determination of the approximate LOC through a calculation procedure simplified that requires knowledge of the LEL and the stoichiometry of reaction (Crowl et al. 2002).

2.2.3 Auto-ignition Point (AIT)

The auto-ignition temperature is, conventionally, the minimum temperature of a heated surface, in correspondence of which, under specified conditions, takes the ignition of an ATEX (Fig. 2.2.3.1).

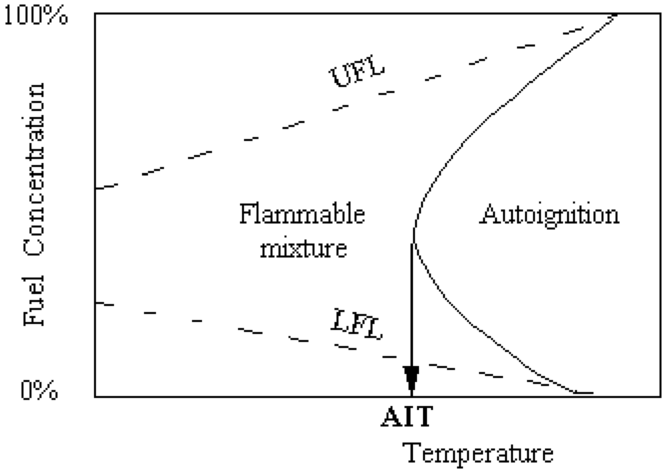


Fig. 2.2.3.1: *Auto-ignition point.*

The gases and vapors present a single ignition temperature (Ti) while the combustible dusts present two types of ignition temperatures: the ignition temperature of a cloud of dust (T_{cl}, cloud temperature) and the ignition temperature of the layer of powder (T_{layer}). It should be noted that this parameter is not an aspect uniquely definable and experimentally detectable, but not being of interest in the evaluation is only mentioned. In general, the ignition temperature tends to decrease with the increase of the hot surface exposed to the ATEX and increases the speed with which the ATEX hugs the hot surface. Furthermore, there are substances that exhibit different ignition temperatures depending on the material with which they come into contact. The legislation to which reference is made for the execution of the test is the UNI EN 14522 (for gases / vapors) and CEI EN 50281-2 (for dusts). This parameter is crucial for the identification of the maximum surface temperature of the appliances (electric and non-electric) placed and designed to operate in potentially explosive atmospheres.

2.2.4 Minimum Ignition Energy

The lowest energy required to cause the ignition of the flammable mixture is called MIE (Minimum Ignition Energy), it occurs at a specific concentration of the substance in the air and is evaluated in the test conditions specified. A source of ignition with an energy equal to MIE is said effective). It is for both gas, vapors and combustible dusts, a sensitivity ignition index useful for sizing equipment of intrinsic safety and for the risk assessment of electrostatic ignition. The minimum ignition energy in the case of vapors and mists, is dependent on the conditions of temperature and pressure to which the mixture is subject. In general, this parameter is proportional to the pressure, similarly to the temperature (Moorehouse et al., 1974) . The MIE, in the case of combustible dust, is correlated to the particle size; the finest tend to own lower ignition energies than coarse dust. This parameter also tends to decrease with:

- The temperature increase of the mixture;
- Increasing the percentage of oxygen;
- The reduction of moisture in the dust.

The test procedures designed to evaluate the MIE, in particular in the case of combustible dust, are made through two different experimental mode: with or without inductance in the test circuit.
Experimental tests of MIE are developed according to ASTM E582 for gases and vapors and UNI EN 13821 for dust.

2.2.5 Flash point temperature

A flammable liquid to participate in the chemical reaction of combustion must pass from the liquid state to a vapor state, therefore it can be said that the index of greater than or lower combustibility of a liquid is supplied from the ignition temperature. The flash point (FP) is one of the parameters used for the classification of flammable liquids. The FP is therefore the minimum temperature at which, in the test conditions specified, a liquid releases a sufficient amount of combustible gas or vapor capable of igniting at the moment the application of a source of ignition effective. There are many devices for the determination of this parameter: the liquid is heated slowly and periodically is applied a weak flame in the area of the vapors; the FP is the temperature at which it generates a flash in the area of the vapors triggered. In general, in a first approximation, it corresponds to the lower limit temperature (TLI) defined as the temperature at which the liquid will vaporize, in saturation regime, with a concentration of steam corresponding to the LEL [MERARD, 1999].

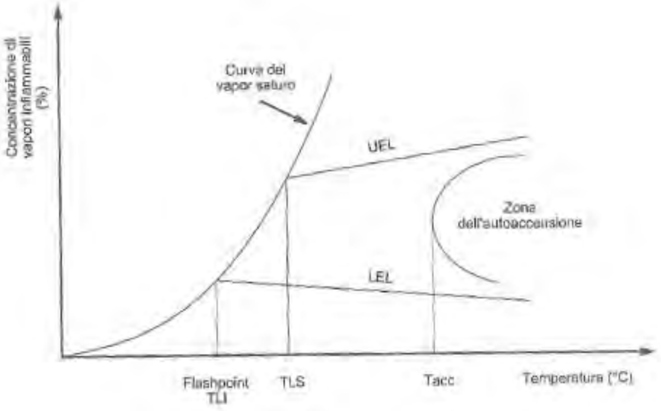


Fig. 2.2.5.1 : *Connection between flammability properties.*

Another important parameter which allows a thorough evaluation of ATEX level of prevention inside of the storage tanks with the method of the saturation of the vapors, is represented by the Upper Limit Temperature (TLS), which represents the temperature at which the vapors saturated reach a concentration equal to the UEL (Fig.2.2.5.1). In the case of flammable liquids storage tanks, the internal condition of prevention is obtainable, then, only in the case where the storage temperature is sufficiently higher than the TLS or lower than the TLI; in these cases, in fact, the vapor concentration is outside the explosion range LEL-UEL and vapors present are not bootable (MERARD, 1999; Ortolani, 1997). Even large excursions of the environmental temperatures may cause an increase in the risk: for example mixtures saturated above UEL stored in tanks, inert under atmospheric conditions, can generate ATEX internal to the field of explosion in the case of a marked decrease of the environmental temperature. The flash point is historically the main parameter useful in selecting attitude flammability of liquids. Starting from the flash point, the law in fact provides for both the labeling and in the safety data sheets you specify the flammable substances / mixtures. Particular attention must be paid to the parameters of pressure and temperature that characterize the presence of the substance and / or mixture in the production cycle. It appears possible that the process parameters classified as ATEX according to Regulation EC / 1272/2008 can make locally non-flammable a substance with a particular risk phrase. On the contrary, it is possible that liquids not classified according to the same regulation, can generate explosive atmospheres. In fact, plenty of fluids even with high flash point, when finely dispersed, exhibit the same characteristics of ignition of their vapors. The case of the mixtures represents an exclusive scenario infact, for example, assuming a binary mixture, the Flash Point does not necessarily lies between the flash points of the individual adjustment components. In the case of azeotropic mixtures, the vapor of the preparation may be greater than that of the individual components, and the flash point lower then. Another aspect to consider is related to the level of contamination of flammable used in the production cycle; the presence of low boiling components can indeed cause a radical change in the characteristics of flammability of the preparation, worsening the risk of fire/explosion. The main standards for determining the flash point are the UNI EN 22592 (open cup test) and UNI EN 22719 (closed cup test). There are not, however, standards internationally recognized for the determination of the upper and lower limit temperature.

2.2.6 Burning rate

A further useful parameter to characterize the risk due to explosions is the burn rate of the laminar and the speed of the flame front. The laminar burning velocity (S_u) represents the speed of propagation of the flame measured at the maximum of combustion gases expansion while the speed of the flame front (S_f) includes the expansion effect of such gases according to the following relationship (Genova et al., 2001):

$$S_f = E \cdot S_u$$

where E parameterizes the expansion of the combustion gases.The laminar speed varies according to the boundary conditions (pressure, temperature, concentrationof flammable liquid). The more relevant the release of ATEX from which originates the flame, the more the flame front will accelerate due to thermal expansion of the burnt gases.

2.3 Regulatory framework

2.3.1 ATEX Directive

At national level, the social directives and product of the European Union in the field of explosive atmospheres (ATEX) were implemented in 2003 thanks to the following measures:

- *Product Directive 2014/34/EU* for the regulation of equipment intended for use in areas at risk of explosion; The directive is aimed at manufacturers of equipment intended for use in areas with potentially explosive atmospheres and is manifested by the obligation of certification of these products; Directive 94/9/EC is from this repealed with effect from 20 April 2016;
- *Social Directive 99/92/EC* transposed in the first legislative decree. N. 626/1994 and now in Title XI, Decree. N. 812008, for the safety and health of workers in explosive atmospheres; It applies in

environments subjected to risk of explosion, where plants and certified equipment are ready for use and thus relates to the users.

Tab. 2.3.1.1.: *ATEX Regulation 94/9/EC.*

<table>
<tr><th colspan="8">ATEX 94/9/EC
Correspondance between zones and categories</th></tr>
<tr><th colspan="2">Group I
[Underground mining, methane and combustible dust]</th><th colspan="6">Group II
[Surface, gas/air or mixture of dust/air, vapors]</th></tr>
<tr><th colspan="2">Category M</th><th colspan="2">Category 1</th><th colspan="2">Category 2</th><th colspan="2">Category 3</th></tr>
<tr><td>1</td><td>2</td><td>G [Gases, Mists vapors **Zone 0**]</td><td>D [Dust, **Zone 20**]</td><td>G [Gases,mists vapors **Zone 1**]</td><td>D [Dust **Zone 21**]</td><td>G [Gases, mists vapors **Zone 2**]</td><td>D [Dust **Zone 22**]</td></tr>
<tr><td>**Equipments ensuring a very high level of protection. Guaranteed operations in case of possible errors**</td><td>Equipments ensuring a high level of protection in case an explosive atmosphere occurs, operation interruption is possible.</td><td colspan="2">Equipments ensuring a very high level of protection. Explosive atmospheres are present continuously for long period or frequently.</td><td colspan="2">Equipments ensuring a high level of protection. Explosive atmospheres are likely to occur.</td><td colspan="2">Equipments ensuring a normal level of protection. Explosive atmospheres are unlikely to occur or, if they do occur, are likely to to do so only infrequently and for a short period only.</td></tr>
</table>

This legislation reveals links and interconnections particularly deep. A first “bridge” between the Title XI, Decree. N. 81/2008 and Presidential Decree n. 126/1998 is given to Part B of Annex L, Legislative Decree. N. 81/2008. It specifies, in fact, that, within the areas classified and extended, must be taken appliances (electric and non-electric) with a category of resistance at ignition suitable to the type of area classified as follows and in Fig. 2.2.6:

- In zone 0 or zone 20, category 1 equipment;
- In zone 1 or zone 21, category 1 equipment or Category 2;
- In zone 2 or zone 22, category 1 equipment, 2 or 3.

A second link between the two regulatory areas is provided by the general philosophy of approach to the problem ATEX: both the employer (Title XI, Decree. N. 81/2008) and the manufacturer (Presidential Decree no. 126/1998) must in fact make reference to or the same principles. This comparison between the two legislative provisions highlights a common approach to security explosion that goes back to the following principles:

- Avoid during operation of the equipment and work training ATEX extended and classified;
- Where this is not possible, it prevents that the potential ignition sources become active and effective;
- In the remaining situations where not even this requirement is feasible, provide protection against explosions.

An explosive atmosphere in accordance with Directive 94/9/EC is defined as a mixture:

i) of flammable substances in the form of gases, vapors, mists or dusts;
ii) with air;
iii) in certain atmospheric conditions;
iv) in which, following ignition, combustion spreads to the entire unburned mixture (note that - especially in the presence of dust - not always all combustible material is consumed by the combustion).

An atmosphere which could become explosive due to local conditions and / or operational is called a potentially explosive atmosphere. It 'just to this kind of potentially explosive atmosphere which are intended products covered by Directive 94/9/EC. The atmospheric conditions considered for the purposes of the definition of an explosive atmosphere provide an oxygen concentration of approximately 21% and reference levels of pressure and temperature, respectively, equal to 101.325 Pa and 293,15 K. Compared to the reference values of pressure and temperature, are permitted variations, provided that they do not affect significantly the explosive properties of the substance flammable or combustible. In this regard, the Guidelines of the European Community for the application of the Directive 94/9/EC suggest to consider, for applications, a range around the reference values of 0.8 bar and 1.1 bar for the pressure and equal to 20 ° C and 60 ° C for the temperature. The combustion air is the substance at which the fuel burns; in our case it is the oxygen contained in the air in a percentage of about 21% by volume. The substances, which combined with the air can cause the exothermic reaction of said explosion are flammable, with the exception of the dust, for which it is preferred to use the term fuels: with these meanings will be indicated from this point on these substances. Flammable liquids are classified, for security purposes and in accordance with the Ministerial Decree of 31 July 1934, based on the flash point (T_i) in:

- *Category A*: highly flammable liquids. T_i <21 ° C. They are the most dangerous products as extremely flammable even at room temperature and must be kept away from possible triggers;
- *Category B*: flammable liquids have a flash point between 21 and 65 ° C;
- *Category C*: (T_i > 65 ° C).

Inks products at Huber Italy are classified, according to the ministerial decree of 31 July 1934, under Category A. Directive 94/9 / EC, as product directive, may in each case relate to the marketing of a wide range of devices simple or complex systems of autonomous protective, assemblies of equipment, components, devices etc. For this reason, the manufacturer will not always be able to know all the characteristics of the product or of the final plant to which the product will do their own part. In these cases it is understandable the limit of the manufacturer in carrying out the principles of integrated explosion safety. The evaluation of the risk of explosion in fact, must take into account in general of the dangers inherent in the overall system due to:

- Equipment, protective systems and components themselves;
- Interaction between equipment, protective systems and components and the substances covered;
- The industrial process made specific equipment, protective systems and components;
- Interactions of individual processes in different parts of equipment, protective systems and components;
- The surrounding environment equipment, protective systems and components and the possible interaction with the processes neighbors.

For this reason, even after the explanations provided by the European Commission, it is considered as a measure imperative to the manufacturer the so-called "assessment of the danger of ignition", notwithstanding the possible need to consider additional security measures (in terms of security integrated explosion) resulting from the necessary exchange of information between the manufacturer and the user.

2.3.2 Classification of the area in an explosive atmosphere

The classification of areas at risk of explosion is a useful method to analyze and classify the environment where they could form an explosive atmosphere. This operation facilitates, therefore, the adoption of measures of prevention and protection in relation to the type of classified zone. It is thus possible to avoid effective ignition sources are located in such areas, with the choice of equipment with an adequate level of protection and take appropriate security measures of technical and organizational. This classification, shown in Table 2.3.2.1, is in Schedule XLIX of D.çgs. n. 81/2008 and are derived directly from defnizioni included in the technical standards CEI EN 600079-10-1 and IEC 60079-10-2 and IEC 60079-102.

Tab. 2.3.2.1 : *Definition of explosive areas according to ATEX regulation.*

Type of Area	Description
0	Area in which an explosive atmosphere for the presence of gas is present continuously or for long periods or frequently (art. 3.6, IEC 60079-10-1)
1	Area in which an explosive atmosphere for the presence of gas is likely to be occasionally present during normal operation (Art. 3.8, IEC 60079-10-1)
2	Area in which an explosive atmosphere due to the presence of gas is not likely to be present during normal operation but, if this is done, it is possible to persist only for short periods (Art. 3.8, IEC 60079-10-1)
20	Area in which an explosive atmosphere from dust, in the form of a cloud of dust in the air, is present continuously, or for long periods or frequently (Art. 6.2, II period, CEI EN 60079-10-2)
21	Area in which an explosive atmosphere from dust, in the form of a cloud of dust in the air, it is likely to occur occasionally in normal operation (Art. 6.2, III period, CEI EN 60079-10-2)
22	Area in which an explosive atmosphere from dust, in the form of a cloud of dust in the air, is not likely is present in normal operation but, if it occurs, it will persist for only a short period (Art. 6.2, IV period, CEI EN 60079-10-2)

For "normal operation" means a situation in which the operation is within the design parameters comprising the steps of starting and stopping; they do not include failures that require repairs and stops. In the international arena we have been proposed various tools for the classification of areas at risk of explosion, both for gases, vapors and mists is for combustible dust. Are cited, without limitation, the following regulatory agencies:

- The European Committee for Electrotechnical Standardization, EU - EN standards produced by CENELEC;
- Energy Institute, UK - IP standards;
- The American Petroleum Institute, USA - Rules API;
- National Fire Protection Association, USA - NFPA Standards.

In Italy is the Italian Electrotechnical Committee (IEC) whose task is to implement the requirements of EN and that provides for its application integration and contextualization through the publication of guidelines. Even in the face of regulatory references are no longer in force, the obvious intent of the Community legislature (first) national and (later) was to direct the employer to a widespread use of the standards of the series EN 60079-10 for the classification of areas at risk of explosion. In this sense, the families of classification standards issued by the various committees regulators prevednìono types, shapes and distances of the areas at risk of explosion is sometimes very different from each other. However, the fulfillment of the requirements of Title XI, Decree. N. 81/2008 requires the preferential use of technical standards and guidelines developed by CEN and CENELEC (EN). Figure 2.3.2.1 is a representation indicative of how the various organizations of international education have addressed the issue of classification of a fixed roof tank (production situation in the area) with containment basin, safety valve and spillway of accidental spills.

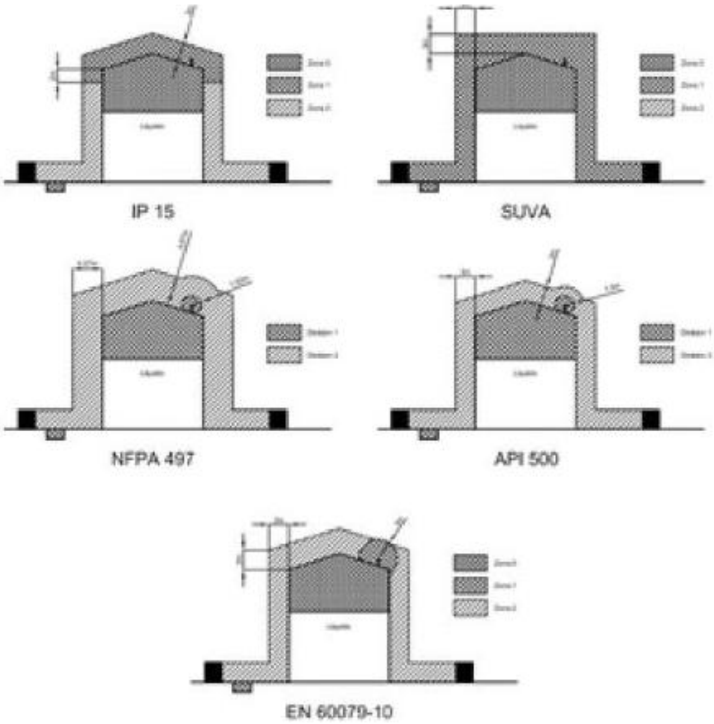


Fig. 2.3.2.1: *Comparison between the various types of classification of a fixed roof tank, equipped with safety valve, the containment basin and duct the exhaust of spills.*

The EN 60079-10-1 is based on the effects of ventilation and in particular on the degree of ventilation and proposes an analytical method by which it determines the type of zone.

The guide CEI 31-35 is based on the European standard and proposes a method for the evaluation of the extension of the area. Similarly with the dust, for which the standard EN 60079-10-2 proposes a method not analytical, wherein the zone type is determined based on the probability that happens a dangerous atmosphere, while its extension is predetermined and It depends on the zone type. The guide CEI 31-56 proposes, instead, a more elaborate method that leads to the determination of the extent of area. Subsequently it will be applied this method for the quantification of possible emissions.

European standards (EN 60079-10-1 and EN 60079-10-2) identify at least three different types of emission sources which, taking place during the production cycle, can give rise to areas classified ATEX.

Tab. 2.3.2.2 : *Source of emissions according to EN 60079-10-1 and EN 60079-10-2.*

Typology	Description
Continuous	The emission of ATEX occurs frequently or for long periods as part of the production cycle. It is normally present inside the containment of process where can be generated gases, vapors, mists (eg. atmospheric tanks, reactors process) or combustible dust in suspension (eg. silos, conveyors).
Of first degree	The emission of ATEX occurs periodically or occasionally during normal operation and can originate both inside and outside of the containment. Typical examples are the safety valves in the case of gases, vapors and mists, or the loading zones FUBC in the case of combustible dust.
Of second degree	The emission ATEX is not present during normal operation and if it occurs it is possible only infrequently. In the case of gases, vapors or mists, it is often associated to failure and seals of flange wear and / or improper maintenance of the gasket or, in the case of combustible dust, in the presence of layers in storage not managed with periodic appropriate cleaning.

From the identification of the degree (or degrees) emission source directly derive the classification of the place where the emission source is located. The preparations necessary for the classification of areas at risk of explosion are therefore as follows:

1. Identify the plants and the stages of the production process object of analysis;
2. Identify the dangerous substances in the production cycle and their physical state.
3. Identify the workplace each potential source of release;
4. Assign each emission source identified the (i) degree (s) of emission (Tab. 2.3.2.2).

2.4 Ignition sources

Under Article. 289, paragraph 2, of Legislative Decree. N. 81/2008, including strategies aimed at preventing explosions are generated in the workplace, prevention of ignition sources is one of the measures most frequently adopted. Moreover, the art. 290, paragraph 1, D.Lgs.81 / 2008 provides that in the assessment of risks, the Employer gives due consideration to the presence of ignition sources within ATEX. The UNI EN 1127-1 identifies as many as 8 sources of power, listed in the following paragraph, that can be correlated with triggers ATEX extended.

2.4.1 Hot surfaces

In industry there are described several scenarios that may give rise to localized overheating, but can be summarized in two families:

- Hot surfaces due to normal operation of the process;
- Failures in mechanical and electrical parts.

The devices that can generate triggers as a result of dysfunction are electrical appliances, pumps, centrifugal fans, compressors, bearings, rotary valves, screws, clutches, brakes, steps tree, radiators, dryers, tube sliding.

2.4.2 Flames and hot gases

The presence of flames and hot gases is incompatible with any ATEX zone classified as the flame temperature is always well above the ignition temperature of any mixture ATEX. The presence of fire in the classified sites may be due to various causes:

- Sigarette smoking unauthorized;
- Electric arc;
- Grinding;
- Oxyacetylene welding;
- Preheat flame;
- Perform electrical work on the EC-ATEX equipment;
- Use of internal combustion engines;
- Heating resistance;
- The presence of vehicles in hazardous areas.

The exclusion of such sources of ignition, while it can be easily obtained during the phases of normal operation of the production cycle through engineering measures, information of workers, safety signs and procedures, it seems more difficult to implement when it is necessary to perform a bypass temporary security procedures (eg. maintenance work, changes of cycle, etc.).

2.4.3 Mechanically generated sparks

Sparks of mechanical origin means the generation of hot particles due to the application of mechanical energy of solid bodies. The presence of sparks in the workplace, although resulting from a multiplicity of operating situations, can be summarized in the following three cases:

- Sparks due to mechanical friction (eg. Mechanical failure to a machine with moving parts);
- Sparks caused by operations with abrasion (eg. Grinding, cutting flexible);
- Sparks due to impact (eg. Collision of particles with the impeller of a fan).

2.4.4 Power Supplies

The trigger due to electric material is connected, during normal operation, to the presence of glitter between the electrical contacts of the switches during their opening / closing or, in case of failure, the presence of short-circuits or overloads that may determine both triggers electrical and overheating.

2.4.5 Electrostatic Discharge

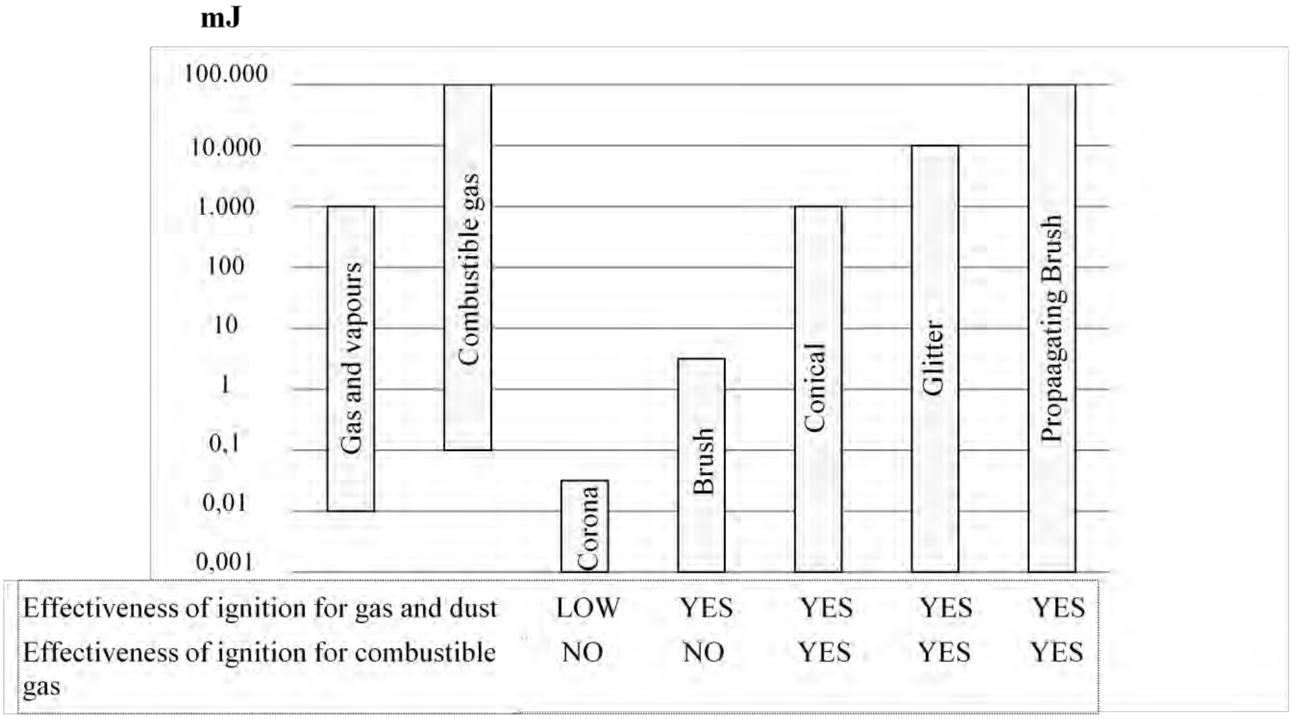
The study of cases of industrial accident includes electrostatic discharge (ESD) among the most common sources of ignition ATEX. The generation of static electricity is present in many industrial processes and is generally caused by:

- Contact and separation of solids (including loads due to sliding and friction and Triboelectricity);
- Flow of liquids or powders and manufacture of spray;
- Electrostatic induction due to the presence of an electric field.

ESD considered are listed as part of the guideline CEI CLC / TR 50404 and are as follows:

- Glitter;
- Corona discharge;
- Brush Discharges;
- Propagating Brush Discharges;
- Conical Discharge.

They generally produce the electrostatic discharge when the intensity of the electric field exceeds 3MV / m (breakdown voltage ina ria) or if the surface reaches the maximum charge density equal to 2.7 · 10-5 C / m_2. However each of the discharges listed has a different capacity to trigger the ATEX as it can be seen from Fig. 2.4.5.1.



	Corona	Brush	Conical	Glitter	Propaagating Brush
Effectiveness of ignition for gas and dust	LOW	YES	YES	YES	YES
Effectiveness of ignition for combustible gas	NO	NO	YES	YES	YES

Fig. 2.4.5.1: *Ignition effectivness of electrostatic discharge.*

2.4.6 Lightning

Lightning can be a cause of ignition, especially in areas classified as type 0 or 20. For such zones, defined hazardous by CEI 81-10, it should be assessed the risk of electric shock. The CEI 81-10 indicates, however, some exceptions because, despite zone 0 or 20, it excludes the risk of explosion if:

- The volume concerning the zone 0 or 20 does not exceed the limits set by the guidelines CEI 31-35 and CEI 31-56;
- No possibility of direct lightning strikes in the area with danger and are prevented in these areas due to shock hazard fraction of the lightning current or eddy current.

In areas inside of the containment conditions, mentioned in previously, occur when:

- The container is able to perform the functions of organ uptake and conduction of lightning currents, which may occur in the area where the container is installed, without giving rise to overtemperatures on the inner surface of the container itself capable of triggering the explosion;
- Inside the container there are no internal systems or are otherwise no measures to prevent shock hazard.

2.4.7 Electromagnetic waves

In the industrial field may be present various sources of emission of electromagnetic radiation. Emissions are divided into the following categories (Table 2.4.7.1): principal electromagnetic emissions in working places.

Tab. 2.4.7.1: *Main electromagnetic emissions present in the workplace.*

Type of electromagnetic emission	Characteristics	Typical industrial application
ELF, VLF, LF	$f < 300$ kHz $\lambda > 1$ km	metal detectors, video terminals, appliances, power lines, telephone lines

Radiofrequenze (RF)	300 kHz f < 300 MHz $1 \text{ m} < \lambda < 1 \text{ km}$	broadcasting, welding, bonding, induction heating
Microonde (MW)	300 MHz f < 300 GHz $1 \text{ mm} < \lambda < 1 \text{ m}$	Radar, telephone, cellular, microwave ovens, radio
Infrarosso (IR)	$700 \text{ mm} < \lambda < 1 \text{ mm}$	Thermal sources
Visibile	$400 \text{ nm} < \lambda < 700 \text{ nm}$	Laser
UltraViolet (UV)	$10 \text{ nm} < \lambda < 400 \text{ nm}$	Sterilization

In addition there are sources of emission within the scope of the Legislative Decree. N. 81/2008, need further evaluation (EN 50499).

2.4.8 Optical, InfraRed (IR) and UltraViolet (UV) radiation

In the visible, IR and UV, the ignition of the ATEX is due to the activation of mechanisms other than those of radio frequencies. Such radiation may be present in devices for measuring and monitoring, ray barriers, measuring a distance, optical fibers used for the transmission of dati.le optical fiber in case of breakage may cause a risk of ignition in conjunction fractured end (conversion of 'energy into heat). It is for this reason that the transmission via optical fiber can not be considered intrinsically safe. The trigger modes of ATEX are three topologies:

- *Resonant absorption*. In the case of IR radiation the emission energy is absorbed dall'ATEX (gases, vapors, mists) with increase of heat while in the case of UV can be activated by a trigger mechanism photochemical;
- *Ignition due to laser*. In the case of the issue consistent and low divergence typical laser it is achieved specific power of the order of 800-1000 MW/cm^2 able to trigger any type of ATEX;
- *Absorption of heat in solids.* The increase in temperature of a surface irradiated by an optical radiation depends on the absorption properties and thermal conductivity of the material, in case there are involved solid materials fuels, it is possible that this first heating ports to the combustion of the solid and subsequently ignition of the ATEX surrounding.

2.5 Measures Of Prevention And Protection

Measures of prevention and protection applicable and following the assessment of ignition sources reported following result from the application of the Decree. N. 81/2008 and have a general validity. Specific measures are set out in the harmonized technical rules to which it belongs the UNI EN 1127-1 which is mentioned in Schedule XLIX, Legislative Decree no. 81/2008. The general provisions applicable, placed in the hands of the employer, are shown below.

2.5.1 Protection Measures

Protection measures provide for the limitation of the effects of the explosion to an acceptable level by means of constructional measures (in this case it is accepted the eventuality of the explosion). They consist of:

- Explosion-resistant design.
- Drain the explosion.
- Suppression of the explosion.
- Prevention of the spread of flame and explosion**.**

2.5.2 Prevention Measures

Preventive measures are those whose aim is to reduce the probability of occurrence of the explosion. Anyway, they reduce but do not eliminate the probability of an explosion, it is therefore almost always necessary to also adopt protective measures. This can be achieved by:

- Replacement or reduction of the amount of substances capable of forming explosive atmospheres.
- Limitation of the concentration.
- Inerting by means of inert gases (nitrogen, carbon dioxide, noble gases).
- Minimizing emissions of flammable substances.
- Dilution ventilation.
- Avoid accumulations of dust.

The prevention of deflagration and detonation may be accomplished by inerting, or a procedure in which the concentration of oxygen present in the air is reduced by the addition of inert gases to a value below the limiting oxygen concentration (LOC).

Chapter 3. The context of the study. Analysis of the current situation

3.1 Company spotlight

Hubergroup is an international group consisting of 40 companies spread across the world. The group is recognized as a leading manufacturer of ink and is in possession of the necessary know-how to produce and sell printing paints, fountain solutions, additives and auxiliaries for printing and actually has the support of a specialized team and updated more than 3,600 employees who contribute directly to the achievement of a production capacity of over 340,000 tons of products a year. A company privately owned for 250 years has constantly redefined its quality standards through an intensive research and development and continues to be a market leader in the production of inks for offset printing and packaging printing.

Fig. 3.1.1: *Huber Italia S.p.a.*

The multinational devotes a lot of attention from time to sustainability through measures designed to reduce energy consumption and to rationalize use of solvents in its production lines. Research and use of raw materials from renewable sources and use of reusable containers and / or recyclable materials are already practice in their manufacturing processes. The Company has developed an internal system of quality management in compliance with UNI EN ISO 9001: 2008, moreover, aware of the growing sensitivity on collective respect and safeguard of the environment and the need to ensure a level of health and safety in the workplace more and more efficient, has decided to implement a system of managing health and safety company according OHSAS 18001: 2007 and an environmental management system according to UNI EN ISO 14001: 2004. It adopts an integrated management system that is based on some basic principles:

- Develop company-wide "culture" of quality, environmental protection and the protection of the safety and health of workers, including contractors;
- Search for the optimization of business processes in order to achieve the highest level of effectiveness and efficiency, while respecting environmental protection;
- Improve their operating procedures for the prevention of possible environmental pollution; help reduce the risks associated with the transport and management of chemicals, ensuring the safety and limiting the impact on the road system;
- Favor partners who share policy Huber Italy SpA safety, health and environment and verify, through the control of their work, which maintain conduct consistent;

- Establishing and reviewing quality objectives, environmental protection and the protection of the safety and health of workers to prevent the risks of major accidents;
- Make available to stakeholders its Policy of Integrated Management.

Environmentally, Huber Italy has obtained the following certificates of conformity:

- Certificate of compliance OHSAS 18001 110302-2012-AHSO-ITA-ACCREDIA;
- Certificate of compliance UNI EN ISO 9001 2008 11591-2007-AQ-ITA-SINCERT;
- Certificate of compliance UNI EN ISO 14001 2004 110644-2012-AE-ITA-ACCREDIA.

3.2 Planimetric description

The company is located in an area of 48.000 m^2, 18.000 of which are covered, divided in three areas as follows, in order to avoid disturbing that can be during the production or in the event of an accident:

- Plant 1;
- Plant 2;
- Caretakers house.

Fig. 3.2.1: *Eye view of the company.*

Plant 1 is mostly dedicated to the mixing, grinding and refining process of raw materials (Fig. 3.2.2) and then, in the remaining one, are located offices and a laboratory. Plant 2, in addition to the production area, hosts a storage for water based and solvent based inks, a raw materials warehouse and a pigments warehouse (Fig. 3.2.3).

Fig. 3.2.2: *Production area.*

Fig. 3.2.3*: Ink's* W*arehouse.*

Each plant is divided into bays, used for the production of inks. Each processing tank is equipped with a localized suction system for the conveying of vapors to a suction pipe and then to the after-burner for their abatement; the ventilation system in operation at the time, is described specifically in Section 3.4. Of lesser extent, but of considerable importance, are the buildings housing the fire prevention tank, the waste collection area, the local boilers, generators, machine and the fire stations with motor pumps units and electric UNI / 9490 containing also the machines for the storage and generation of the foam. Outside the two factories, twelve cylindrical silos serves as solvents storage (Fig. 3.2.4), located in two separate containment basins, placed to clear sky, volume range between 2 and 10 m^3. The tanks are built in AISI / 304 (stainless steel) , equipped with manual and automatic plant for cooling of the external surfaces with off via filming foam monitors controlled by UVR detectors. In the top of the tanks is installed the system and siphoning vent with formation of saturated air into the top. To communicate directly with the atmosphere, also the outer surface is reflective to prevent solar rays to penetrate; alongside the twelve external tanks, pumps, located in a room protected by foam systems aspires solvents measuring withdrawal.

Fig. 3.2.4: *Silos for sovents storage.*

Finally, separate from the others, a bunker, constituted by two rooms built in reinforced concrete, houses the deposit of nitrocellulose used in the initial production phase.

3.3 Production cycle

Printing inks are made of four basic components:

- *Pigments* - to colour the ink and make it opaque;
- *Resins* - which bind the ink together into a film and bind it to the printed surface;
- *Solvents* - to make the ink flow so that it can be transferred to the printing surface;
- *Additives* - which alter the physical properties of the ink to suit different situations.

The pigments and nitrocellulose flakes are stored in bags or big-bags of varying weights while solvents are stored in twelve cylindrical silos placed outside the plant, each of volume between 15 m^3 and 22 m^3. To help the dispersion of pigments in solvents, it is used various type of resins and in some types even nitrocellulose, nitric ester of cellulose, that is wet at 35% in ethanol in order to prevent its drying and so avoiding to activate its explosive hazard (its characteristics are reported in *Chapter* 3.5). The production cycle occurs in three phases:

Step 1 - Varnish manufacture

Varnish is the clear liquid that is the base of any ink. Different varnishes are made for different inks, but they are all made by mixing the resins, solvents and additives (often at high temperatures) to form a homogeneous mixture. The resins react together to some extent to make larger molecules, making the varnish more viscous the longer these reactions are allowed to occur. This phase takes place in the mixing station (Fig. 3.3.1a)), consisting of a mixer, into which can be introduced various types of solvent from the distribution lines.

Fig. 3.3.1: a) *Mixing station; b) Detail of the agitator and hatchway.*

Step 2 - Pigment dispersal

The pigment is mixed into the varnish and then ground in a grinding mill (Fig. 3.3.2) to break up clumps of pigment and to spread them evenly through the ink. The introduction of the pigments is by the mean of manual loading containers or big-bags through a hopper located on a hatch (Fig. 3.3.1 b)) ; these systems are supported by special electronic scales, properly calibrated, weighing the compound and blocking the spillage weight reached. During the spillage of substances, the operator directs, in correspondence of the hatch, the mechanical arm connected to the suction system (Fig. 3.3.3) in order to avoid inhalation and volatilization in the work environment of powdery substances; this protective meaure is required by law. Of fundamental importance is the type of exothermic nature reaction that is created inside the reactor that with the addition of pigments and nitrocellulose causes an increase of temperature up to about 40 °. As dispersion begins, also the mechanical work of the agitator, transfers to the mixture, the thermal energy allowing the constant maintenance of the temperature reached and thereby allowing to reach the homogeneity of the half – processed product. The duration of this initial phase is about two hours.

Fig. 3.3.2: *Grinding mill.*

Fig. 3.3.3: *Mechanical arm connected to the suction system.*

Step 3 - Finishing

After around two hours, the semifinished product is pumped to the finishing reactor. The finishing stage is the last step in ink's production, having variable duration, typically one or two days, depending on the type of ink produced. In finishing reactors, to maintain the semifinished product under conditions of low viscosity, through a part of the energy produced by the post-combustion, they are heated and maintained at a temperature slightly higher than that in the initial phase, about 55/60 ° C. As emptying is completed, two coolers produce cold water in order to cool the reactors and the grinding mills and make them available to the next production.

The laboratory is primarily involved in quality control, although it is also involved in designing special ink formulations for unusual printing situations. Inks are tested for a variety of properties during and after manufacture process. Most of the tests are dictated by their end use. Typical tests include:

- Non volatile content
- Viscosity
- Dispersion
- Shade
- Adhesion
- Slip
- Scratch resistance
- Gloss
- Flexibility
- Water resistance
- Heat Resistance
- Opacity

3.4 Plant description

During the production cycle, the reaction between the pigments, resins and solvents produce gas such as ethanol, methanol etc .. that must be evacuated to protect the health of workers, to prevent air pollution and avoid the creation of explosive atmospheres on workplace. In areas used for the ink manufacturing,above the process reactors, it is installed a plant for extraction and abatement of airborne dusts and volatile organic compounds divided in the following way (according to Fig. 3.4.2):

- Line 1 (dusts and vapors collected together), red coloured, located only in the emission points. Process reactors for ink's manufacturing, in which combustible dusts are used, are located in the following areas: Plant 1-Bay 1,2,3,4,5,6; Plant 2, Bay 1. Each point of aspiration of powder state substances requires an air flow rate of 750 m^3/h, therefore 26,500 m^3/h for dust suction, since 35 points are present in the plant 1. In the plant 2, ink's process reactors in which is used the powder are in amounts significantly less, therefore, through the inverter, the suction fan works at the 50% of its nominal load, that means 9,000 m^3/h. The two fans, designed according to the flow rates given above, are driven by inverters and equipped with suitable control unit exchange for the management of alternation, connected to the flow control system to that activate the second fan in case of failure of the first one. Upstream, a filter for the abatement of dusts is installed (Fig. 3.3.3); after filtration, the purified air is collected to the “clean” one, then conveyed together to the furnace by the mean of a single pipeline;

- Line 2, light-blue coloured, 14.000 m^3/h and 5.000 m^3/h for Plants 1 and 2 respectively, but equipped only with a control flow valve for adjustments according to the actual needs.

The system’s design is equal to the previous one. The Fig. 3.4.1 and 3.4.2 below show a lay-out and a picture of the entire suction line.

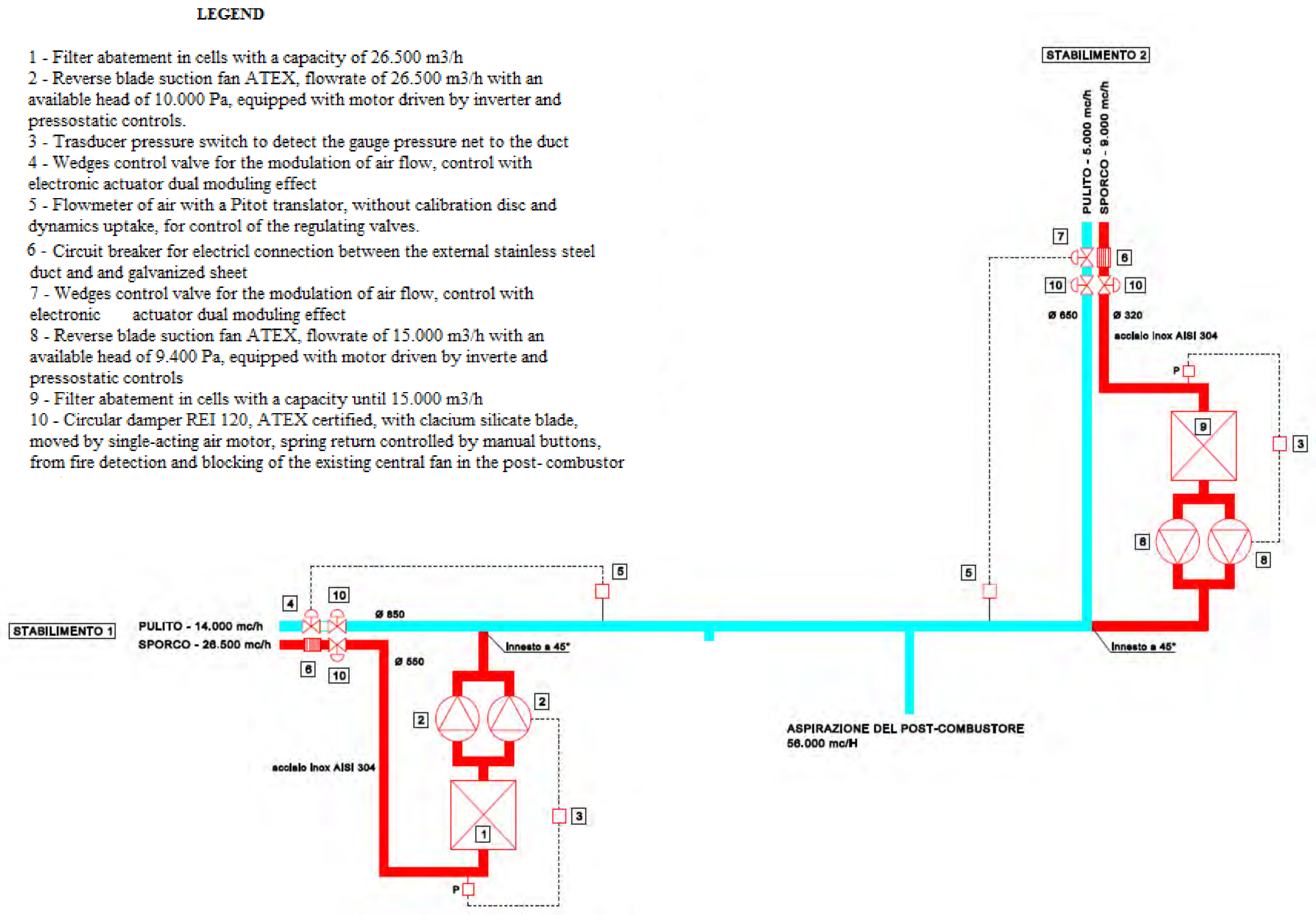


Fig. 3.4.1: *Aspiration system lay-out.*

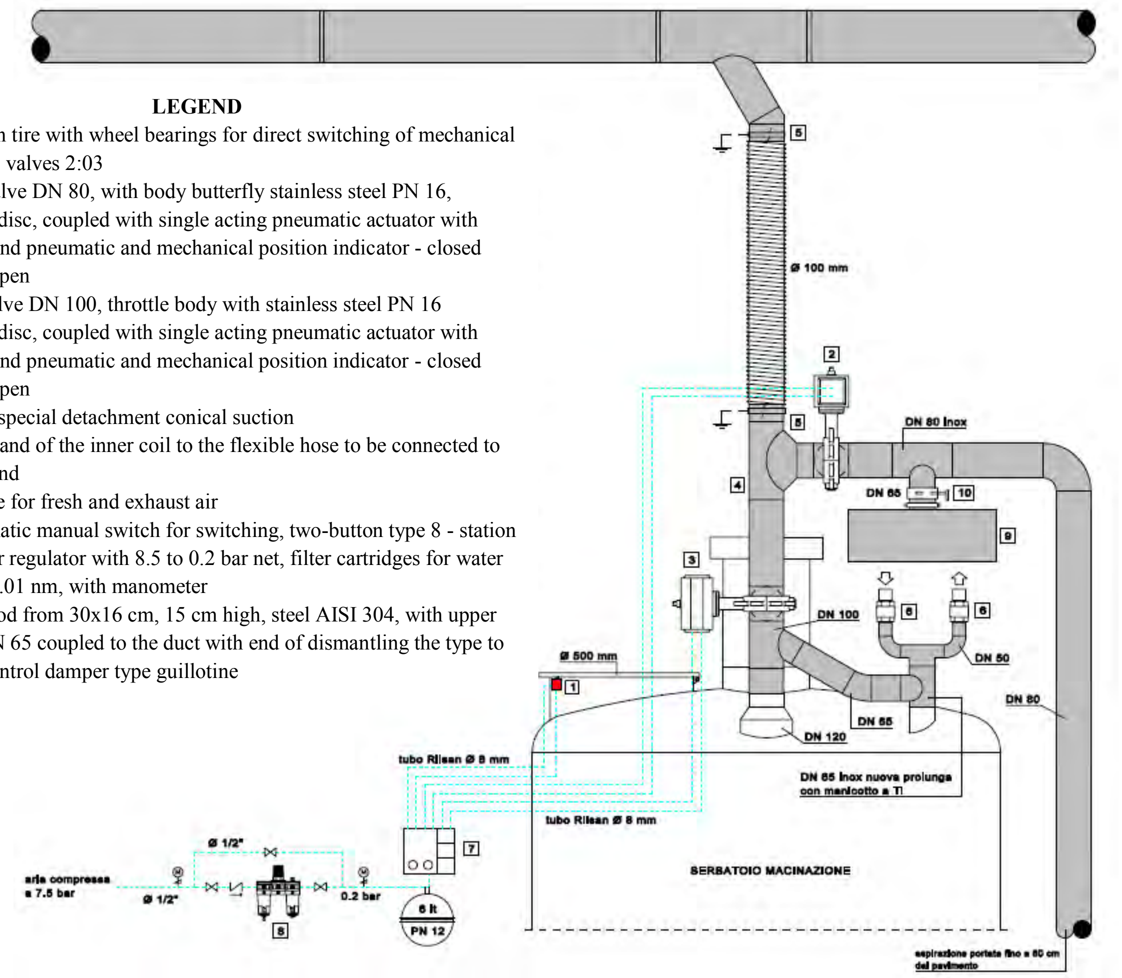
LEGEND

1 - Filter abatement in cells with a capacity of 26.500 m3/h
2 - Reverse blade suction fan ATEX, flowrate of 26.500 m3/h with an available head of 10.000 Pa, equipped with motor driven by inverter and pressostatic controls.
3 - Trasducer pressure switch to detect the gauge pressure net to the duct
4 - Wedges control valve for the modulation of air flow, control with electronic actuator dual moduling effect
5 - Flowmeter of air with a Pitot translator, without calibration disc and dynamics uptake, for control of the regulating valves.
6 - Circuit breaker for electricl connection between the external stainless steel duct and and galvanized sheet
7 - Wedges control valve for the modulation of air flow, control with electronic actuator dual moduling effect
8 - Reverse blade suction fan ATEX, flowrate of 15.000 m3/h with an available head of 9.400 Pa, equipped with motor driven by inverte and pressostatic controls
9 - Filter abatement in cells with a capacity until 15.000 m3/h
10 - Circular damper REI 120, ATEX certified, with clacium silicate blade, moved by single-acting air motor, spring return controlled by manual buttons, from fire detection and blocking of the existing central fan in the post- combustor

Fig. 3.4.2: *Main air pipeline.*

To better permit the balancing and calibration of the two branches of each plant, downstream of each group of fans of the two sleeve filters, is placed a balancing damper operated manually. The damper ensures that it is equal depression of the two branches present in each of the two junctions between the vapor line and the other one. Diameters of the input suction pipes to the filters is 520 mm, corresponding a minimum of internal speed of 25 m / s guaranteed constantly during all phases of operation of the plant. This value must be ensured in order to avoid dusts deposit in the pipe; these deposits would be a potential source of explosion since nitrocellulose dusts in drying conditions become an hazardous source (explained in *Paragraph* 3.5). To ensure that the flow rate and hence the speed never falls below this value, but to allow to close the suction towards the inside of sinks without that the pipe portions or the collector have decreased flow (and therefore speed livelihood), the system is provided with a system of descent, which simultaneously closes the valve towards the sink and opens a suction valve ambient air.

Fig. 3.4.3: *Reactor process equipped with aspiration system.*



LEGEND

1- Microswitch tire with wheel bearings for direct switching of mechanical and pneumatic valves 2:03
2- Butterfly valve DN 80, with body butterfly stainless steel PN 16, stainless steel disc, coupled with single acting pneumatic actuator with spring return and pneumatic and mechanical position indicator - closed with tank lid open
3- butterfly valve DN 100, throttle body with stainless steel PN 16 stainless steel disc, coupled with single acting pneumatic actuator with spring return and pneumatic and mechanical position indicator - closed with tank lid open
4 - piece with special detachment conical suction
5 - clamping band of the inner coil to the flexible hose to be connected to electrical ground
6 - check valve for fresh and exhaust air
7 - part pneumatic manual switch for switching, two-button type 8 - station compressed air regulator with 8.5 to 0.2 bar net, filter cartridges for water and oil up to 0.01 nm, with manometer
9 - exhaust hood from 30x16 cm, 15 cm high, steel AISI 304, with upper connection DN 65 coupled to the duct with end of dismantling the type to tighten 10 - control damper type guillotine

Fig. 3.4.4: *Technical lay-out of the aspiration system.*

According to ATEX Directive (*Chapter* 2.3) and with reference to the particular shown above, it is emphasized that the valves (2 and 3) and the microswitch (1) are surrounded by an explosive zone. In particular the valve (3) is located in a zone 0 and 20 (category 1GD) and the microswitch in 1 and 21 ones. The section of flexible pipe is of the type with coiled metal core, which is in perfect mechanical contact with the fixed piping upstream and downstream , and clamps to ensure electrical continuity; the overall resistance to earth of any point of the hose is below 10^6 Ohm. The ambient air inlet DN 80 is provided with flame arrester network and can be directed in such a way as to contribute to better the reclamation of the air present within the workplace. The total design air load of the suction plant is 40,000 m^3 / h for the dusts and vapors lines in the Plant 1, and 15.500 m^3 / h for the Plant 2.

Fig. 3.4.5: *Abatement filters.*

The post-combustor consists of two devices: firstly, the vapors, once conveyed to the boiler, via natural gas burners, are brought to temperatures of 600 °, 800 ° and 1000 °; reaching the maximum temperature. Then, the combustion gases pass in countercurrent, through a second device, consisting of ceramic beds, which have the task of absorbing the energy contained in the flue gases in order to reuse it for the continuous treatment of the"vapors" line arriving from the pipe . Upon cooling, the fumes are emitted into the atmosphere through the chimney at about 250 ° / 300 ° C in accordance with legal limits.

Fig. 3.4.6: *Details of the furnace.*

Fig. 3.4.7: *Chimney.*

3.5 System's preventive and protection measures

For both lines, the following requirements, prevention and protection measures, are met:

- The filters for the abatement and suction lines are made of steel suitably resistant against corrosion. In the contact points between different materials it is guaranteed the perfect metallic continuity;
- The electrical resistance between the parts of the plant from the first suction point to the last filter protection of the afterburner and from any point to the ground is always less than 10^6 ohm;
- The internal parts in contact with the sucked effluent (paint, anti-rust) and the internal surfaces of equipment next to or internal explosion zones, are free of coatings;
- All plants are constructed in such a way that failure of a component to wear (bearings, fans, valves, filter sleeves, sensors, ..) does not cause the loss of availability of the ventilation. With this purpose, there are provided redundant fans that never allows the reduction of the flow for each line to below 75% of nominal flow.
- A possible black-out must not cause loss of the effectiveness of ventilation; in realizing the electrical system of exhaust systems therefore there have been prepared frameworks so that they can be fed through a prime line which maintains in tension, in case of blackout, at least the suction fans, for the time necessary to the interruption of all dangerous emissions.
- To permit verification of the presence of any stratifications of powders, spaced hatches are available for quick inspection of the piping.
- To prevent the formation of explosive atmospheres due to vapors, detectors of concentration of VOCs are installed on each line that monitor the concentration of solvents in continuous.
- The detection system s are provided with double threshold; to pass the first threshold activates an alarm signal (in a safe area and the remote permanently manned) which mobilizes the process of securing (lids locking, emissions interruption) for the branch which presents the anomaly. On exceeding the second threshold, it's activated the bypass command which sends all gaseous waste directly into the atmosphere without going through the afterburner. In order to ensure redundancy of detection and control of the correct operation of the instruments installed, there is an additional detector SOV placed downstream of the main manifold in which are combined all four suction lines that guarantees not exceeding the limit concentration in entrance to the afterburner.

  In addition, for the lines "Vapors and dusts" containing both dust fumes, are implemented the following measures:

- The micro switches used for direct switching of pneumatic valves and mechanical two-way are certified ATEX 94/9 and marked Ex "2G IIIC T95 ° C IP6X". The two-way pneumatic valves are certified ATEX 94/9 and marked Ex "2G IIIC T95 ° C IP6X".
- A detection system with spark extinguishing water system is installed for each suction line powders, upstream of the station abatement, with subsequent second cell detection sparks for verification of switch-off. The nozzles are connected to the ring spark off the fire by pipeline suitably protected against freezing winter.
- The abatement filters installed are of the multi section type with the sleeves replaceable without interruption of the operation.

The filters and the parts subjected to excess explosion pressure (pipes, input and output of the filters, check valves, airlock, screw conveyors, fans, basket door sleeves ..) are designed so as to withstand the stresses expected during a possible explosion in view of cost reduction systems of pressure explosion installed. The criterion used for sizing of the members and for the selection of mechanical components to be installed is the type EXPR (Explosion Pressure Shock Resistant). The characteristics of the powders that can participate in the explosion are to be considered in relation to the characteristics of explosion of the nitrocellulose shown in Fig. 3.5.1 below:

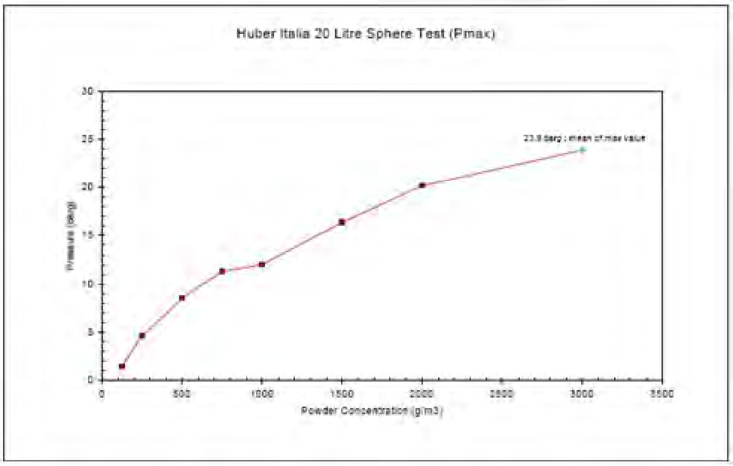


Fig. 3.5.1: *Pressure rise vs. dust concentration.*

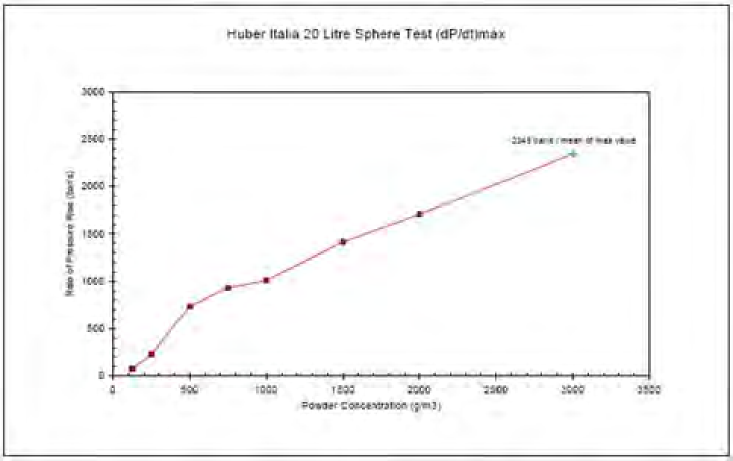


Fig. 3.5.2 : *Rate of pressure rise vs. dust concentration.*

Following are the values obtained in the test report _S102293R1V1 of Chilworth Technology and data of P_{Max} and K_{st} of dust and nitrocellulose are extrapolated to various concentration. P_{max} represents the destructive power of a dust the explosion develops; Kst is a measure of the nitrocellulose speed of the explosion pressure increase, in other words, also gives an indication of the rate of expansion of the flames associated with the explosion. The analysis has been performed on a sample as dried, ground and then sieved dust, in order to have a grain size less than 63 micrometers. This procedure, required by law, offers particular representativeness of the actual conditions that are established in the filter in which the effect of the flowing air dust naturally tends to dry out and in which the particles of higher granulometry tend to fall in the discharge hopper, whilst the finer ones remain more in suspension. Red indication states the value chosen for the subsequent sizing of the installations of extraction and abatement. For security purposes, it has been considered that the P_{Max} = 12 bar and the Kst = 300 bar m / s are reached at a concentration of 300 g / m^3 equal approximately to 1/3 of the concentration of 1.000 g / m^3 to which are obtained such values for these parameters.

Tab. 3.5.1: *Response of test report _S102293R1V1, Nitrocellulose explosiveness.*

Concentration	P_{max}	(dP/dt)m	Kst
g/m^3	barg	bar/s	bar m/s
125	1,4	75	21
250	4,6	230	63
500	8,5	738	201
750	11,3	930	253
1000	12	1008	274
1500	16,4	1416	385
2000	20,2	1710	465
3000	23,9	2345	637

- In order to ensure that the explosion characteristics remain those indicated above and to ensure that you go with forming a cloud of dust in a concentration in excess of such values, is the cleaning of sleeves so, during this operation, it must be guaranteed its timing in order to ensure that the quantity of suspended dust and, therefore, the dust concentration is kept below the design limits.
- The filters were designed and installed by providing a system of explosion "venting"; each panel is equipped with an alarm signaling device in case of opening of the membrane vent in order to stop in the event of explosion the operation of the fans.
- To prevent the propagation of the explosion upstream of the abatement, at the entrance of each filter is installed a check valve of the explosion to be placed on the intake manifold upstream of the filter. It is guaranteed that the pressure P reached on the non-return valve in case of explosion is less than / equal to the pressure limit of the non-return valve (normally P_{lim} of the valve is equal to 0.5 bar). It is emphasized that the section of tubing between the non-return valve of explosion and the filter is properly sized to resist the excess pressure which develops in case of explosion due also to the intervention of the valve.
- **T**o avoid or at least limit the propagation of the explosion downstream of each abatement filters, they have a distance d in meters of pipe from subsequent parts of the plant calculated according to the following formula:

$$d = 10\,V \cdot x^{\frac{1}{3}}$$

where V is the internal volume of the filter. The portion of tubing up to this distance is dimensioned and secured to withstand the overpressure explosion produced.

- The filtering devices are made of antistatic materials and in direct contact with the corresponding metal supports in order to ensure the continuity of the system ($R < 10^6$ ohm).
- There is an instrumentation to that verify the clogging of the filter by means of differential pressure gauge, between upstream and downstream of the filtering system which generates appropriate signal and in case of excessive decrease of the speed inside the ducts, interruption of the system.
- To prevent the formation of explosive areas in case of breakage or deterioration of filtering devices is provided a suitable detection system dust inside the suction pipe downstream of each filter; the system is equipped with an alarm (acoustic-bright) set on two thresholds, the first signaling (occurrence of dust) will need to check and dissect the stretch of the filter in which the loss has been found, in the case of the extended alert or the achievement of a certain concentration of dust (less than 25% LEL, about 10 g / m^3), will instead turn off the system and / or the sending of the gaseous effluents to the fireplace bypass without passing through the afterburner.
- In order to ensure that there are no leaks even downstream of the Fabric Filters and to ensure the proper operation of the detectors listed in the previous paragraph, there is an additional detector

powders leaving the bag filter itself which is calibrated at lower thresholds but that possesses operating principle entirely similar to the previous one.

- Control system of the filling level of the hopper (internal, zone 20; external 22).
- Fire detection system inside the filter that gives an alarm in the area "safe" and permanently manned by which it will be possible to activate a shutdown system to flooding of the filter.
- In order to allow shutdown of a possible outbreak of fire in the filter is an appropriate nozzle system for flooding, correctly designed and installed in accordance with the regulations in force.The system is designed for the implementation of both automatic and manual flooding. At the automatic implementation of the system of flooding, the suction fans are instantly switched off and all the fire dampers upstream and downstream of the filter in which the anomaly occurs closed. The system must guarantee eliminate or at least minimize false alarms and thus any unnecessary intervention of the system of flooding. With this purpose, there are two sensors for detecting fire places inside the filters. Only in case of detection by both sensors it is automatically activated the system of flooding while, with only a sensor that detects the fire, is sent an alarm signal;
- Exhaust system of the filtered product which conveys the material into a container by means of rotary valve which guarantee suitable compartmentalization against explosion. Discharge takes place preferably in big bags (FIBC-Fexible Intermediate Bulk Container, type C) and must be provided with detection system level (categorized 1D 3G) to prevent overfilling and/or the formation of cloggings.
- Technical room has been realized in sandwich panel with transparent door access and skylight for internal control, where to place the bags during filling. It is equipped with fire detection and extinguishing system conceptually designed as that referred at the point previously mentioned (automatic start / manual and dual-detector system which, however, one of rise and a smoke, driven by the same logic and activating also the fan retainer and the closure of fire dampers) appropriately categorized 3GD. In the outside area, the conveying line is equipped with special water protection systems against freezing at least until the solenoid valve, also certified in category 3GD. The internal fire ring for the room is equipped with nozzles discharge (at least 2 k60) and external connection points are present for connection to the water mains fire. The electrical systems inside the unloading local (lights, motors, sensors, fire, ...) is cathegorized 3 GD for zone2/22. All equipment components of the plant, as well as expressed in each point, are classified as follows:

A) The inside area of the sinks until the pneumatic valve exchange, is classified as zone 0 and 21;
B) The section of pipe between the pneumatic valve of sharing of each sink and the main pipe is classified as zone 1 and 21;
C) The main pipe upstream of the stations abatement zone is considered "clean."
D) The "dirty" area of filters to be installed is classified as zone 20.
E) The installed and all the systems downstream of the afterburner areas are kept clean;
F) The area outside the filter area is considered as a "clean" zone (not hazardous) always to compliance with appropriate maintenance and regular checks.
G) The discharge area of the powders FIBC class C is to be considered zone 20 internally to the FIBC and 22 externally.

The suction line in the plants 1 and 2 comply with the specific standards and product directives, in particular:

DIRECTIVE ATEX 94/9 / EC
MACHINERY DIRECTIVE 2006/42 / EC
LOW VOLTAGE DIRECTIVE 2006/95 / EC

DIRECTIVE 2004/108 / EC ON ELECTROMAGNETIC COMPATIBILITY
UNI EN 14491
UNI EN 13463
UNI EN 14797
UNI EN 1127-1
CEI CLC TR 50404
CEI EN 60079-29 Components of the detection system
CEI EN 50402 Detection System

Following in Tab. 3.5.2 are the data related to the mass flow rate of total volatile organic compounds derived from the analyzes carried out to chimneys during the current operation:

Tab. 3.5.2 : *Current air flowrates.*

Maximum mass flow rate	**125 Kg / h**
Mass flow average	275 Kg / h
Mass flow idling	35 Kg / h

The concentration in ducts under "ordinary" conditions for nitrocellulose is less than 100 mg / m^3. To satisfy the emission limits required by current legislation, filtering devices are sized according to BAT (Best Available Technologies), having abatement efficiency of about 99% for particles of particle size less than 0.2 μm. Moreover, whereas the operation of three shifts, the entire system does not exceed stringent noise limits in the area (40 dB at night house of the nearby neighbors) .

The extinguishing system in the areas used for production is of foam coating type, agent on the machines, in addition to the sprinkler type with high foam dispensing.The maintenance of the emergency is fundamental to the functionality and success of applying the safety rules of the system. The monitoring and maintenance is carried out periodically by staff, together with monthly shutdown and updating drills.

Chapter 4. Fire Risk Assessment

4.1. Introduction to Fire Prevention and Protection (FP)

The "Fire Prevention" is the discipline that studies, implementing measures, devices and modes of action to prevent, report and reduce the probability of occurrence of a fire and in any case to limit their consequences for people and the environment. The methods of fire prevention, therefore, pay particular attention to the factors that affect the causes of the onset of the fire.

It is established that the fire prevention has a different cost depending on the stage in which it applies:

- Work in design;
- Work in progress;
- Work realized.

Except in cases of force majeure, fire prevention must be made during the design phase of the work. To reduce the likelihood of a fire, it is necessary to identify the risk factors for people and things, assess the level of risk, and thus eliminate the various causes. Moreover, to reduce the damage, once the event has occurred, in order to contain within certain limits the energies released by the fire, it is necessary to modify the conditions of propagation of combustion, creating difficulties in the combustion and by detecting in the shortest time possible to act before the "flash over" and allow the evacuation of people.

This process allows the employer to take the necessary measures effectively to protect the safety of workers and other people in the workplace and include:

- Prevent the risk of fire;
- Information of workers and of the people;
- Training for workers;
- The technical and organizational measures intended to put in place the necessary measures.

The "Fire Protection" is the discipline that deals with measures to minimize, in space and time, the damage caused by a fire in order to limit their consequences. The protection measures fires can be of two types:

I. *Passive protection*: structural features, functional and topological of any hazardous fire, prepared for a preventive measure for the safety of life in the event of fire and to confine the propagation of combustion. Are those measures provided for in the design phase in the broadest sense of the word and that are activated not by the action of the person automatically incident.
   For example:
   - Reduction of fire load
   - Creation of a suitable partitioning, an adequate fire resistance of premises and facilities;
   - Use of materials of furniture with appropriate class of fire resistance;
   - Design of appropriate escape routes and safe places within the building to be designed.

II. *Active Protection:* set of facilities and fire fighting equipment, prepared in relation to the nature of the risk under the criteria of fire prevention, which can be activated manually and / or automatically to the onset of the fire and aim to contrast the spread of the flames and reach the extinction of the fire.

For Example:

- Automatic fire detection systems;

- Extinguishing manuals (fire extinguishers, hydrants networks, etc.) Or automatic; Smoke and heat extraction systems, automatic or manual.

Preventing fires is directly linked to a proper assessment of fire risks in the workplace. The latter consists essentially of: identifying hazards, identify the people involved, to finalize the risk assessment and estimate the level of risk. The evaluation of the risk of fire is strictly linked to the type of activities and materials stored and handled, but also the equipment on, including the furnishings, the construction characteristics of the workplace and coating materials. It is therefore clear that in order to assess the risk of fire, it is necessary to preliminarily analyze the factors that characterize the process of combustion. Actually, the company examined, implements all kinds of active and passive protection. In this chapter, it is quantified in numerical terms the level of residual risk to which the factory is subject, which is defined as the level of risk remaining even though are applied devices, preventive, active and passive protection measures.

4.2 Specific regulatory frame work

The relevant legislation on the fire risk in the workplace was represented by the Legislative Decree n. 81 of April 9, 2008, better known as the "*Testo Unico*", and Ministerial Decree 10/03/1998, entitled "General criteria for fire safety and emergency management in the workplace". The Legislative Decree no. 81/08 includes a number of requirements, intended for employers, on the prevention and protection from such risk within the company. The provisions contained in the T.U. relate to various aspects, such as:

- Appointment of firefighters;
- Presence of appropriate signage;
- Conditions and number of fire extinguishers;
- Provision of fire escapes;
- Monitoring extinguishing systems.

As a result, in particular, they have reported other decrees which discipline in detail the fire risk.

4.2.1 D.M. 30/11/83. "Terms, general definitions and graphic symbols of FP"

This provision can be considered as a starting point, in terms of fire prevention theme, to define the structural characteristics of a company subjected to fire and explosion risk. Indeed, it aims to give general definitions relating to specific expressions of FP in order to achieve a uniform application of the rules drawn up in accordance with the decree of the President of July 29, 1982, 577. In particular, for the purposes of a uniform language and uniform application of the rules drawn, it is defined the fire resistance of structures as aptitude of a construction element (component or structure) to store, according to a predetermined temperature program and for a determined time in whole or in part, the *stabilit*y R, the *seal* E, the *thermal insulation* TI, defined as follows:

- *R*: Ability of a building element to retain their mechanical strength under the action of the fire;
- *E*: Ability of a building element to not let pass or produce (when subjected to fire on one side) flames, vapors or hot gases on the unexposed side;
- *TI*: Ability of a building element to reduce, within a given limit, the transmission of heat.

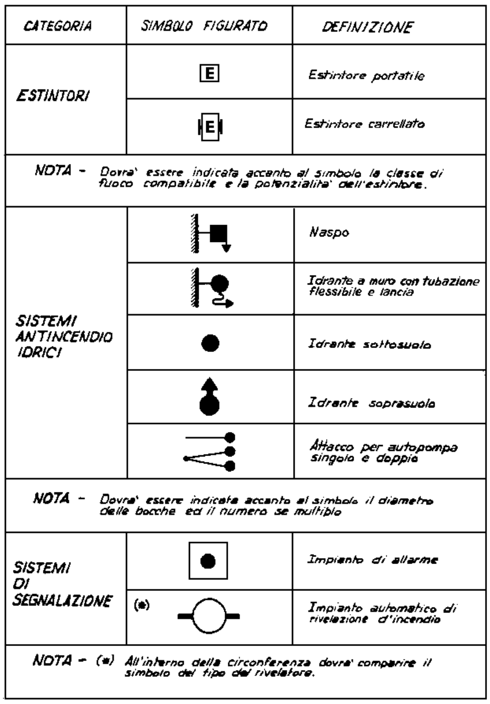
The structural elements will therefore be the subject of the following classes of fire resistance:

REI RE R   15 30 45 60 90 120 180

where the number indicates, in minutes, the time during which the element should maintain, if exposed to a standard fire in the oven experimental, the required characteristics.
For which:

- REI 15 indicates that the constructive element must retain stability, tightness and thermal insulation for 15 minutes first, and so on;
- RE 15 indicates that the constructive element must preserve the stability and the seal and for 15 minutes first, and so on;
- R 15 indicates that the constructive element must preserve the stability for 15 minutes first, and so on;

There are also introduced the definition of fire load, which will find a more extensive discussion in Circular n. 91/6, and the definition of the various safety distances and other terms relating to the systems of exodus. The Ministerial Decree concludes with definitions related to mobile means of fire extinguishing (fire extinguishers) and fixed fire-fighting (building blocks of networks of hydrants), introducing graphic symbols (Fig. 4.2.1.1) to be taken in the technical drawings and tolerances for measures of various kinds terms and definitions given in fire prevention.



CATEGORIA	SIMBOLO FIGURATO	DEFINIZIONE
ESTINTORI	E	Estintore portatile
	E	Estintore carrellato
NOTA - Dovra' essere indicata accanto al simbolo la classe di fuoco compatibile e la potenzialita' dell'estintore.		
SISTEMI ANTINCENDIO IDRICI		Naspo
		Idrante a muro con tubazione flessibile e lancia
	●	Idrante sottosuolo
		Idrante soprasuolo
		Attacco per autopompa singolo e doppio
NOTA - Dovra' essere indicata accanto al simbolo il diametro delle bocche ed il numero se multiplo		
SISTEMI DI SEGNALAZIONE		Impianto di allarme
	(*)	Impianto automatico di rivelazione d'incendio
NOTA - (*) All'interno della circonferenza dovra' comparire il simbolo del tipo del rivelatore.		

Fig. 4.2.1.1: *Graphic symbols to be taken in tecnica drawings.*

4.2.2 D.M. 16/02/82. "Activities subject to the Fire Department control"

This rule modifies the D.M. 27.09.65 concerning the determination of activities subject to fire prevention inspections. It also decrees the premises, assets, deposits, plants and hazardous industries whose projects are subject to examination and prior opinion of the provincial command of the Fire Department and the exercise of which is subject to examination and inspection for the issuance of the Fire Prevention Certificate (FPC); it is also established the frequency of subsequent visits to the renewal of the certificate. Those responsible for the activities under the decree are required to request in advance the renewal, regardless of the expiration date of the certificates, in the case of:

- New destination of the premises;
- Qualitative and quantitative variations of existing dangerous substances in the establishments and / or deposits;
- Every time they are in the changing security conditions previously accepted.

The transition from the old to the new decree is based on a careful and thorough analysis of the potential risks of fire, taking into account the available statistical data of experience in the activity of fire suppression since 1965 by the National Corps Fire Brigade. In drawing up the new list, it is also given updates due to the technological progress of the last twenty years. In addition to the various activities, both industrial and commercial, have been proposed more precise information based on the characteristics of the treated products and related processes in order to overcome difficulties and uncertainties which occurred in the past. Then, there are also introduced activities that, despite limited risk of fire, are to be considered dangerous for the consequences that events, also of limited relevance, may have because of crowding of people and their intended purpose. In reference to art. 5 Presidential Decree 151/2011 art. 5 DM 7.8.2012, the holder of activities subject to this classification must send to the Fire Command the request for periodic renewal of the compliance period fire every 5 years.

4.2.3 Circular n. 91/61. "Specific fire load calculation and determination of the class"

The standard is intended to provide designers and builders of manufactured civil with steel structure (subsequently extended to industrial buildings) the criteria for proportioning of protection against fire to be arranged in defense of steel structures, so that the burning of combustible material in the building is exhausted before the structures themselves reach temperatures that could compromise the stability and also important in the risk analysis carried out in the next chapter. First it must be considered the fire load to the premises or to the floor in question. Its value is obtained by calculating, for all combustible material present, the equivalent wood on the basis of the higher calorific value of the wood amounts to 4.400 Cal/kg. According to this parameter it is determined a classification of:

Classe15 Classe20 Classe30 Classe45
Classe60 Classe90 Classe120 Classe180 Classe 240

The approximate number of each class expresses the virtual fire load in kg/m^2 of standard wood. This number, also indicative, expresses in minutes the minimum duration of fire resistance from request to the structure or to the construction element in question. The classes are determined by the formula:

$$c = k\,q$$

where:
c number indicative of the class;
q fire load stated by the designer (kg wood/m^2);
k reduction factor that takes into account the real fire of the floor space or in the building complex.

4.2.4 D.M. 10/03/98. “General criteria for fire safety and emergency management in the workplace”

The decree lays down the criteria for the assessment of fire risks in the workplace and indicates preventive measures and fire protection to be taken in order to reduce the occurrence of a fire and limit the consequences if it occurs. There are defined the workplaces to which law is applicable according to the activity carried out, as well as temporary or mobile sites. Then, are list the names of the workers responsible for implementing fire prevention, fire fighting and emergency management or that of the employer. In Annex I, the basic guidelines for the assessment of fire risks are:

- Identification of any fire hazards;
- Identification of employees and other persons present in the places exposed to the risks;
- Elimination or reduction of fire hazards;

- Assessment of the residual risk of fire;
- Assessment of the adequacy of existing security measures or detection of any further steps and measures necessary to eliminate or reduce residual risks fire.

In accordance with these criteria, the employer shall assess the level of risk classifying it in one of the following categories:

a) High risk;
b) Medium risk;
c) Low risk.

The decree also distinguish the two definitions of:

FIRE HAZARD: properties and intrinsic quality of certain materials or equipment, or methods and practices of work or use of a work environment, which have potential to cause a fire.
RISK OF FIRE: probability that of achievement the potential level of occurrence of a fire and occurring consequences on the occupants.

4.2.5 D.P.R. 151/2011. “Rules for the regulation of measures relating to fire prevention”

The Presidential Decree 151/11 (Rules for the regulation of the procedures relating to fire prevention), transposing the provisions of Law n. 122/2010 for the streamlining of administrative, identifies the activities subject to the rules of fire prevention and has simplified the various obligations on the part of stakeholders. DPR 151/11 sets a principle of proportionality, according to which the administrative are diversified in relation to the size, the sector in which the company operates and the actual need for protection of public interests. The new regulation on fire protection updates the list of activities subject to fire prevention inspections and, introducing the principle of proportionality, correlates the same ones to three categories, A, B and C, identified according to the level of risk rather than size or, in any case, the degree of complexity that distinguishes the activity itself.

- *Category A*: activities with 'technical regulation' reference and characterized by a low level of complexity, related to the consistency of the activity, crowding and the quantities of material present;
- *Category B*: activities present in A, as a type, but characterized by a higher level of complexity, as well as activities devoid of a specific technical regulation of reference, but with a level of complexity lower than the assumed parameter for the 'top ';
- *Category C*: activities with high level of complexity, regardless of the presence or absence of 'technical regulation'.

The latest version of the classification of activities subject to fire prevention is provided in Annex III of the DM 07/08/2012. Table 4.2.5.1 shows the activities in the corporate environment, subject to technical visits and inspections by the fire department and their classification according to the above mentioned:

Tab. 4.2.5.1 : *Classification of activities according to the DM 07/08/2012.*

New classification D.P.R. 151/2011 activity n.	**Typology**	**Cathegory**		
		A	B	C
1.1	Factories and plants where they produce and / or employ flammable and / or oxidizing with global quantities in cycle higher than 25 Nm3 / h.			X
10.2	Factories and plants where are produced and / or used flammable liquids and / or fuel with a flash point up to 125 ° C with total quantities in the cycle and / or in storage $\geq 50m^3$.			X
12.1	Deposits and / or resale of liquids with a flash point above 65 ° C, with capacity from 1 to 9 m^3 (excluding flammable liquids).	X		
12.3	Depots and / or retail of flammable liquids and / or fuel and / or lubricating oils, heat transfer, of any derivation, the overall geometric capacity up to 50 m^3.			X
15.3	Depots and / or retail of alcohols with concentration higher than 60% by volume, of geometric capacity more than 50 m^3.			X
17	Factories and plants where we produce, use or hold explosive substances classified as such in the Implementing Regulations of the consolidated public safety laws approved by Royal Decree May 6, 1940, n. 635, and subsequent amendments and additions.			X
21.1	Factories and plants where are produced, used or hold substances liable to spontaneous combustion and/or substances which in contact with water, emit flammable gases.			X
46.2	Factories and plants where they produce and / or use, flammable liquids and / or combustible with a flash point up to 125 ° C, with the total quantities in the cycle and / or storage exceeding 1 m^3.			X
49.1	Groups for the production of electrical energy with subsidiary endothermic engines and cogeneration plants with total power from 25 to 350 kW.	X		
74.1	Equipment for the production of heat fired by solid fuel, liquid or gaseous power equal to 116 kW (up to 350 kW).	X		
74.3	Installations for the production of heat fired by solid fuel, liquid or gas with a potential greater than 700 kW.			X

4.3 Fire Risk Assessment

4.3.1 Introduction to the concept of risk

The risk, according to the D.M. 10/03/98, is the likelihood of injury or damage to health in a hazardous situation; whereas the risk analysis can be defined as the process of evaluation of the possibility of accidents, their probability of occurrence and the analysis of possible consequences. In the chemical industry the risk of operating a plant generally has a high degree of occurrence, because of its peculiarity of producing dangerous substances: hydrocarbons are flammable and therefore can generate fire and explosion; organic liquids can be explosive or thermodynamically unstable, give rise to uncontrolled exothermic reactions, be corrosive or toxic and therefore dangerous if released. There are also the accidental overpressures inside the equipment and the failure of materials and structures. For these reasons, the chemical industry must be considered as a possible theater of major accidents. In principle, the risk assessment consists of four phases:

a) **Identification of fire hazards and people at risk**. Systematic procedure to identify all the hazards associated with products and people involved in it. Once hazards have been identified, it can be changed the project in order to minimize them, whether or not it has been estimated the level of risk. If the danger is not identified, it will not be able to meet them at the design stage;
b) **Risk Estimation**. Determination of the probability that it is realized the identified hazards (and the severity of any damage arising from such dangers, see also EN 1050);

c) **Risk assessment.** Comparing the estimated risk and criteria in order to decide whether the risk is acceptable or whether the product design must be modified to reduce the risk in question;
d) **Analysis of options for reducing risks.** The last phase of risk assessment is the process of identifying, selecting and editing changes to the plan to reduce the overall risk from products.

The starting point of this procedure is, in fact, a risk assessment of the current situation and the proposal of an alternative project that aims to reduce them significantly. This assessment is a "snapshot" of the actual situation. Although it is always possible to further reduce the risks, they can rarely be reduced to zero, if not eliminating activities. This term, named as “residual risk”, is the risk that remains after applying all the procedures for identification, elimination, reduction and control of hazards.

4.3.2 Identification of fire hazards

4.3.2.1 Combustible materials and/or flammable

Combustible materials (cardboard packaging, wood pallets) are present in low quantities in laboratories and in production quantities in the warehouses of discrete storage of finished products and raw materials in the warehouse. These materials properly handled and stored safely, not be the subject of special evaluation.
Flammable materials in significant amounts are deposited in metal containers and metal shelves in special warehouses. Some materials, present in the workplace, are potential danger because they are easily combustible and/or flammable or can facilitate the rapid development of a fire.

4.3.2.2 Centers of danger

There are the following centers of danger:

- Heating plant with 1 - CT / 05-METHANE GAS boilers for space heating BUILDING N.02, total power of 25 kW burned.

4.3.2.3 Ignition sources

The premises in which they are deposited and processed the combustible or flammable materials previously described, there are no particular sources of ignition and heat sources that are potential causes of fire or which may favor the spread of fire. Internal movements are done through electric forklifts led by trained personnel.

4.3.3 Identification of people at risk

In the establishments covered by this report, and in particular in the areas of production, there are situations in which some operators may be exposed to risk of fire due to the treatment or to the materials (flammable solvents and inks). Carefully considered the various cases, will not be that one or more people will be exposed to special risks, in case of fire, because of their specific function or for the type of activity carried out at the place of work. In particular, it will not be provided for:

- The presence of areas of rest;
- The presence of occasional public in a number such as to determine the situation of overcrowding;
- The presence of persons whose mobility, hearing or sight are limited;
- The presence of people who are not familiar with the places and their escape routes;
- The presence of workers in specific risk areas of fire.

4.3.4 Elimination or reduction of fire hazards

As it regards the presence of combustible materials and flammable, both their quantity, both the deposit will entail adoption of particular actions to reduce the danger of fire and in particular:

- Storage of flammable materials in local made with fire-resistant structures.

It is still very careful when depositing combustible and flammable material so as to be separated between the various types available and that materials are deposited neatly on metal shelves, freeing passageways and escape routes. The measures to reduce the dangers caused by heat sources are summarized in the points below:

- Check the conformity of electrical technical regulations in force;
- Control on the correct maintenance of electrical and mechanical equipment;
- Repair or replacement of damaged equipment;
- Identification of the areas where smoking is prohibited and regulations on smoking in other areas;

4.3.5 Fire Risk calculation

To define the residual risk of fire in quantitative terms, it is used the Fire Safety Engineering software **CPI win® FSE**, by “BM Sistemi”,leader program that allows to apply the principles of safety engineering for fire fighting and for the evacuation of people to safe places. **CPI win FSE**, namely Fire Safety Engineering, allows to analyze the spread of fire and study the development of combustion products through the calculation engine developed by NIST. When integrated with the FSE Evac module allows to design and test the escape routes and the security plan correctness. It starts from the following mathematical model, that defines it as:

$$RR = C_i * F_m * F_C$$

where:

C_i Fire load expressed in Kg of wood or equivalent Standard/m^2;
F_m Product of multiplying factors of risk that represent the parameters responsible for the increase in the fire risk. It is the term connected to the MAGNITUDO ;
F_c Factor of risk compensation related with all the parameters that contribute to the mitigation of risk. It is the term connected to the FREQUENCY.

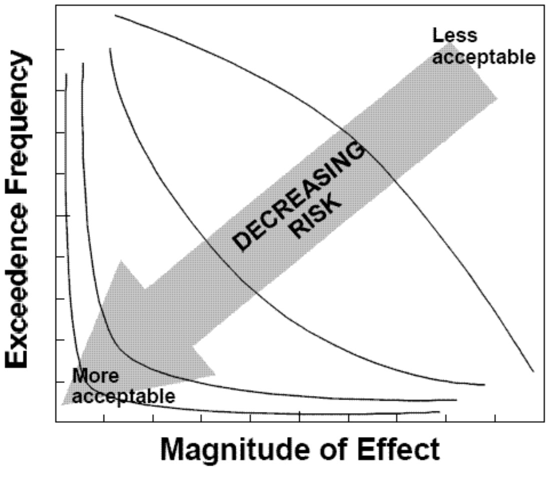


Fig. 4.3.5.1: *Magnitudo and Frequency effect on risk estimation*.

Figure 4.3.5.1 shows how magnitude and frequency influence the risk analysis.

4.3.6 Fire load

The specific fire load rating q_f, expressed in Kg of wood or equivalent standard/m^2, is defined as:

$$q_f = \frac{\sum_{i=1}^{n} g_i \cdot H_i \cdot m_i \cdot \psi_i}{A}$$

where:

g_i	mass of the nth combustible material [Kg];
H_i	lower calorific value of the nth combustible material [MJ/kg];
m_i	factor of combustion of the nth combustible material equal to 0.80 for wood and other cellulosic materials and 1.00 for all other combustible materials;
ψ_i	limiting factor of participation in combustion of the nth combustible material equal to 0 for materials contained in containers specially designed to withstand fire; 0.85 for materials contained in non-combustible containers and are not specially designed to withstand fire; 1 in all other cases;
A	gross layout surface of the compartment [m^2].

The specific fire load of design $q_{f,d}$ is given by:

$$q_{f,d} = q_f \cdot \delta_{q1} \cdot \delta_{q2} \cdot \delta_n$$

Where:

q_1 is the factor which takes account of the risk of fire in relation to the size of the compartment and whose values are defined in the Tab. 4.3.6.1:

Tab. 4.3.6.1: *q_1 factor values.*

Gross layout surface of the compartment (m^2)	**q_1**	**Gross layout surface of the compartment (m^2)**	**q_1**
$A < 500$	1,00	$2.500 \leq A < 5.000$	1,60
$500 \leq A < 1.000$	1,20	$5.000 \leq A < 10.000$	1,80
$1.000 \leq A < 2.500$	1,40	$A \geq 10.000$	2,00

q_2 is the factor that accounts for the fire risk in relation to the type of activity performed in the compartment and whose values are defined in the Tab. 4.3.6.2:

Tab. 4.3.6.2: *q_2 factor values.*

Classes of risk	**Description**	**q_2**
I	Areas that present a low risk in terms of probability of initiation, propagation speed of the flames and the possibility of controlling the fire by the emergency teams	0,8
II	Areas with a low fire risk as probability of ignition, rate of spread of a fire and the possibility of controlling the fire itself by emergency crews	1,0
III	Areas with a high fire risk in terms of probability of ignition, rate of spread of the flames and the possibility of controlling the fire by the emergency teams	1,2

$\delta_n = \prod_i \delta_{ni}$ is the factor that takes into account the different protection measures and whose values are defined in the Tab. 4.3.6.3:

Tab. 4.3.6.3: *δ_{ni} values.*

δ_{ni}, Function of protection measures						
Automatic fire extinguishing	**Evacuation systems**	**Automatic detection,**	**Corporate team**	**Fire mains**	**Protected routes of**	**Accessibility to emergency**

		automatic smoke and heat	**alarm and fire alarm**	**dedicated firefighting**			**access**	**vehicles**
Water system δ_{n1}	Other δ_{n2}	δ_{n3}	δ_{n4}	δ_{n5}	Internal δ_{n6}	Internal and external δ_{n7}	δ_{n8}	δ_{n9}
0,60	0,80	0,90	0,85	0,90	0,90	0,80	0,90	0,90

The level of residual risk, based on the result obtained from the formula given above, can be obtained by applying the following criteria (Tab. 4.3.2.1.4):

Tab. 4.3.6.4: *Criteria for residual risk classification*.

RR	LEVEL OF RESIDUAL RISK
< 20	Low
20-50	Medium
>50	High

4.3.7 Multiplying factors of risk

The multiplying factors of risk are those parameters responsible of fire risk increase. They are directly connected to the concept of MAGNITUDO. The magnitude of the consequences can be expressed for example as a function of the number of parties involved in this type of risk and the level of damage caused to them.

Tab. 4.3.7.1: *Mutiplying factors of risk.*

Multiplying factors of risk		
PARAMETER	**DEFINITION**	**VALUE**
Burning rate	R_c	1,7
Toxicity of the combustion products	P_f	2
Probability of initiation	Pi	1,6
Probability of personal injury	P_{aff}	1

4.3.8 Risk compensation factor

The compensation factor of the fire risk is related to the environmental conditions, the fire safety facilities and management organization of the work, in all aspects of fire prevention. The parameters determining it are identifiable with the responses to each question, their text is reported in separate grids by subject in Annex 1. Each single response contributes for a portion equal to 1/n, where n is the total number of questions. The compensation factor is obtained, then, with the following algorithm:

$$F_c = 1 - \frac{\sum_{i=1}^{10}\left(D_{ok}(P_s)\right)i}{\sum_{i=1}^{10}\left(N_{tot}(P_s)\right)i} = 0{,}06$$

Tab. 4.3.8.1: *Classification of areas according to specific fire load of design.*

Compensation factor	
PARAMETER	**DEFINITION**
D_{ok}	Number of questions with an affermative answer.
N_{tot}	Total number of questions to answer than "QUESTION IS NOT APPLICABLE TO THE SECTOR UNDER CONSIDERATION".

The 10 parameters P_s originating the compensation factor of the fire risk are:

- Probability of initiation;
- Features of the buildings and premises;
- Security operating procedures and working;
- Conditions and likelihood of exodus;
- Maintenance;
- Alarm;
- Antifire;
- Control;
- Security management and emergency;
- Training and information

In addition, considering the estimated fire load, areas are classified according to Tab. 4.3.5.2.

Tab. 4.3.8.2: *Classification of areas according to specific fire load of design.*

Specific fire load of design ($q_{f,d}$)	**Class**
Not greater than 100 MJ/m^2	0
Not greater than 200 MJ/m^2	15
Not greater than 300 MJ/m^2	20
Not greater than 450 MJ/m^2	30
Not greater than 600 MJ/m^2	45
Not greater than 900 MJ/m^2	60
Not greater than 1200 MJ/m^2	90
Not greater than 1800 MJ/m^2	120
Not greater than 2400 MJ/m^2	180
Greater than 2400 MJ/m^2	240

4.3.9 Results

In the following Tab. 4.3.9.1 are shown the protection measures on use and, so, the quantification of the δ_{n7} coefficient:

Tab. 4.3.9.1: *Protection measures as a function of δ_n.*

Description	**δ_n**
Automatic water and foam based fire extinguishing	0,48
Corporate team dedicated firefighting	0,85
Internal and external fire mains	0,8
Protected routes of access	0,9
Accessibility to emergency vehicles	0,9

Then, recalling the definition of Residual Risk (RR):

$$RR = C_i * R_C * P_f * P_i * P_{aff} * F_c$$

The risk level of each area is summarized in Table 4.3.9.2:

Tab. 4.3.9.2: *Characterization of the Residual Risk of each area.*

Area/Sector	**Function**	**Specific fire load of design MJ/m^2**	**Class**	**Residual Risk**
Factory n.1- Bay 1	Production area	3.001	240	61
Factory n.1- Bay 2	Production area	2.747	240	56
Factory n.1- Bay 3	Production area	1.687	120	34

Factory n.1- Bay 4	Production area	4.760	240	98
Factory n.2- Bay 1	Production area	5.451	180	55

Detailed calculations are included in Annex I. The results have been plotted in the following graphs (Fig. 4.3.9.1 and 4.3.9.2):

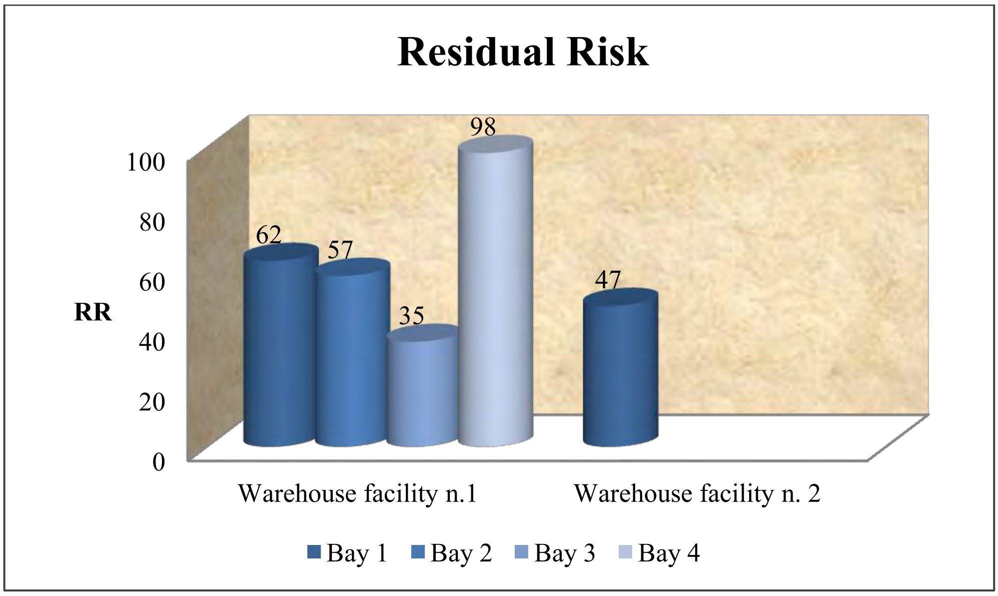


Fig. 4.3.9.1: *Risk quantification.*

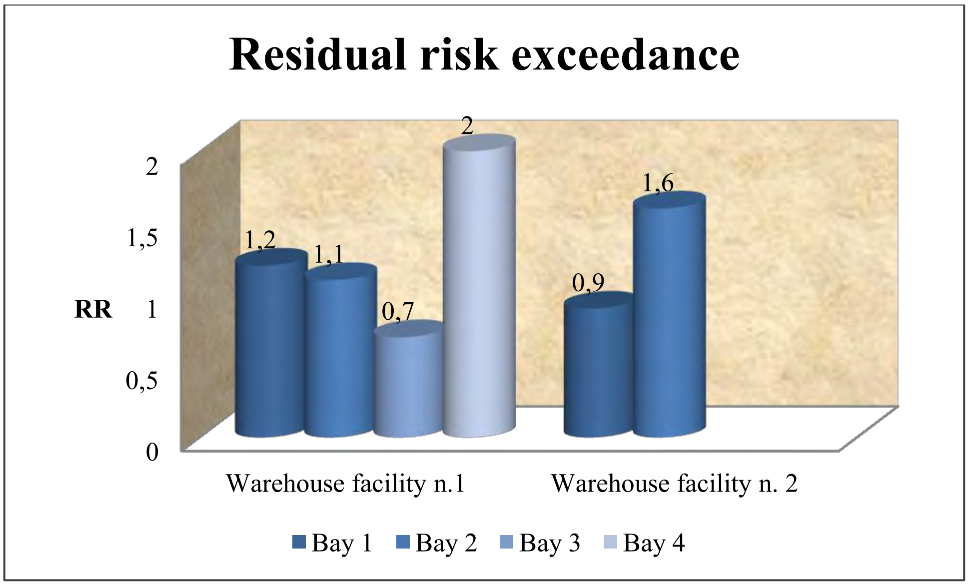
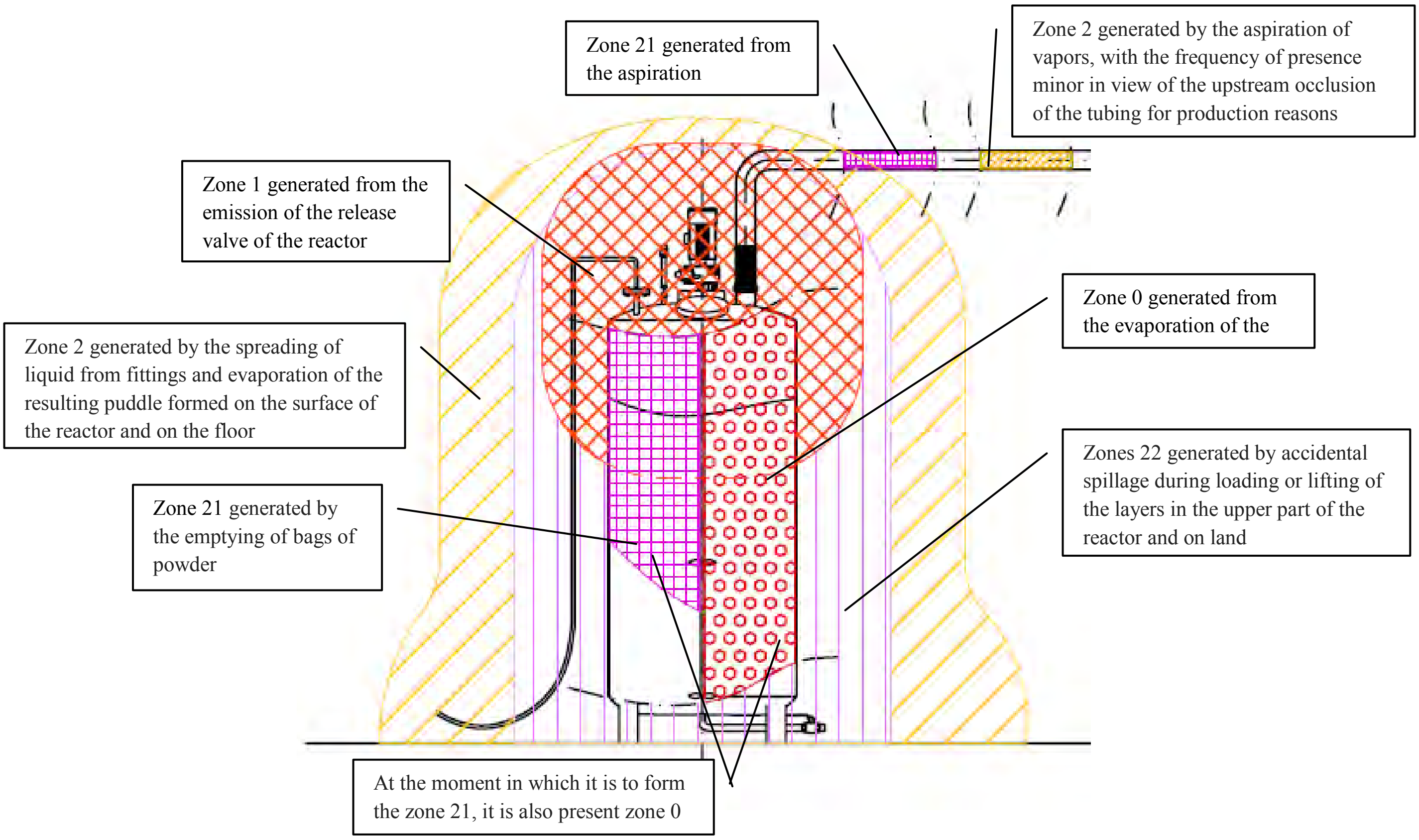


Fig. 4.3.9.2: *Risk comparison to the threeshold value.*

4.4 Classification of areas at risk of explosion

The classification of areas at risk of explosion is a function of the degree of the emission source and the degree and availability of ventilation as indicated in Tab. 4.4.1. The classification of areas at risk of explosion, in and around the reactor, was drawn up in Fig. 4.4.1 according to Tab. 4.4.1.



Zone 21 generated from the aspiration

Zone 2 generated by the aspiration of vapors, with the frequency of presence minor in view of the upstream occlusion of the tubing for production reasons

Zone 1 generated from the emission of the release valve of the reactor

Zone 0 generated from the evaporation of the

Zone 2 generated by the spreading of liquid from fittings and evaporation of the resulting puddle formed on the surface of the reactor and on the floor

Zones 22 generated by accidental spillage during loading or lifting of the layers in the upper part of the reactor and on land

Zone 21 generated by the emptying of bags of powder

At the moment in which it is to form the zone 21, it is also present zone 0

Fig. 4.4.1: *Classification of areas surrounding the process reactor.*

Tab. 4.4.1: ATEX classification matrix.(CEI EN 60079-10-1)

Emission degree	**Ventilation degree**						
	High			**Medium**			**Low**
	Availability of the ventilation system						
	Good	**Appropriate**	**Poor**	**Good**	**Appropriate**	**Poor**	**Good, Appropriate, Poor**
Continuos	(Zone0NE) Not hazardous	(Zone0NE) Zone 2[a]	(Zone0NE) Zone 1[a]	Zone 0	Zone 0 + Zone 2	Zone 0 + Zone 1	Zone 0
First	(Zone1NE) Not hazardous	(Zone1NE) Zone 2[a]	(Zone1NE) Zone 2[a]	Zone 1	Zone 1 + Zone 2	Zone 1 + Zone 2	Zone 1 or Zone 0[c]
Second	(Zone2NE) Not hazardous	(Zone2NE) Not hazardous	Zone 2	Zone 2	Zone 2	Zone 2	Zone 1 and Zone 0[c]
(a): Area 0NE, 1NE or 2NE indicate a theoretical area where, under normal conditions, the extension is negligible. **(b): Zone 2 was a second degree emission may exceed that due to an issue of first degree or continuous; in that case, it should be considered to be the greater distance.** **(c) : It is zone 0 if the ventilation is so weak and the emission is such that an explosive atmosphere for the presence of gas exists practically on continuity (that is, it is close to a situation of "no ventilation".**							

4.5 Need of action

Despite taking all preventive and active and passive protective measures, following quantification of residual risk, it is concluded, according to Tab. 4.3.3, that the production area of the company is currently subject to a high level of risk, which is why it is proposed this project for the inertization of process reactors. For the purpose of motivating the aforementioned need for intervention, it has been studied the chemical composition and the chemical and physical behaviour of the substances used for inks production. In the following paragraphs are studied the characteristics of the vapor phase by defining the parameters related to the explosion risk. The three temperatures to which reference is made to represent the limiting cases of the study are:

T = 10 ° standard conditions at room temperature. Solvents temperature during reactor filling;
T = 45 ° operating conditions in the mixing tank;
T = 65 ° limit conditions of the system in case of failure.

The temperature of 10 °C is studied referring to the worst unfavorable working conditions, that is during winter.

4.5.1 Printing ink chemistry

The ink is a mixture of variable consistency, from liquid to pasty, comprising solutions of dyes or suspensions of pigments in a dispersing fluid and worked with oil, with the feature of fixating on certain materials, such as paper or other suitable media by means of writing, printing or by the use of a stamp. Its chemical composition is as follows:

- Colorants;
- Binders;
- Solvents;
- Addittives.

4.5.1.1 Colorants

Pigment is a natural inert substance, obtained from quarries in India, China, Turkey, and is used to change color to a material; what distinguishes one from a pigment dyes, is its inability to being soluble in common solvents such as water, and that is precisely why the use of particular types of solvent-based alcohols and esters.

⇒ anorganic: titanium dioxide (white), carbon black (black)
⇒ organic: are classified with Colour Index C.I..
⇒ special effect pigments: metallics, iriodines, fluorescent pigments.

Colour shade, transparency and purity are defined by the choice of pigment used and also numerous fastness/resistance properties.

4.5.1.2 Binders

Binders are those chemical substances that cause two other substances to form into one. The ones used are from:

- raw renewable materials: cellulose derivates, rosin derivates. Nitrocellulose, Maleic resin;
- fully synthetic binders: based on crude oil: PVB, PVC, Polyurethane resin, Polyamid resin, Ketone resin, Acrylic resin.

Properties conferred/influenced by the binder system are:

- Pigment wetting;
- Viscosity;
- Ink adhesion;
- Laminate adhesion;
- mechanical resistance properties (e.g. scratch resistance, rub resistance);
- Gloss;
- Solvent retention;
- Sealability, sealing resistance.

4.5.1.3 Solvents

In the following Tab. 4.5.1.3.1 are shown solvents used for ink production and their Evaporation Index, Flash Point and Boiling Point. *The Evaporation Index* provides a representative number which allows to predict the evaporation rate of the substance.

Tab. 4.5.1.3.1: *Characterictics of solvents used for ink production.*

Substance	Evaporation Index	Flash Point (°C)	Boiling point (°C)
Ethanol	8,3	12	78
Isopropanol	8,3	12	82
n-Propanol	16	22	97
Ethyl acetate	2,9	-4	77
Isopropyl acetate	4,2	3	88
Methoxypropanol	22	32	120
Ethoxypropanol	33	42	129
Methoxypropyl acetate	44	44	146
Ethoxypropyl acetate	70	54	158
Methoxybutanol	160	60	161

Properties conferred/influenced by the solvents:

- Solubility properties;
- Drying properties;
- Solvent retention;
- Viscosity:
  - ➯ Delivery viscosity;
  - ➯ Print viscosity.

4.5.1.4 Addittives

Addittives are substances added in order to easily create an high performance to inks and toners and that deliver clear definition, striking visual impact and long-lasting color in flexographic, gravure, digital, lithographic, inkjet and other types of printing.

- Plasticisers: impact the flexibility of the dry ink film, reduce the residual solvent content;
- Adhesion promoters: improve adhesion of the ink film on the substrate;
- Slip additives: adjust the slip properties for finishing;
- Waxes : improvement of mechanical stability and of blocking resistance;
- Matting agents;
- Defoamers: reduce foaming phenomen;
- Anti-static addittives : help to reduce electrostatic charging of films;
- Anti-toning : reduce toning and tramlining in gravure applications.

According to Tab. 4.5.1.4.1, generally the composition of a printink ink is:

Tab. 4.5.1.4.1: *Printing ink's composition*.

Organic pigments	**5 - 20%**
Binders	10 - 20%
Additives	1 - 3%
Organic solvents	50 - 80%

The *Gecko Concept* used to produce inks provides a maximum range of applications with few components and products. It involves a simple and quick formulation, simplified production, a consistently high level of quality, identical ink composition in all markets, condensed and improved know-how. Then the optimized use of resourses leave more room for more service, innovation and development together with the costumer.

4.5.1 Type of inks products

In detail, the production of ink concerns three types shown in the following Tab. 4.5.1.1:

Tab. 4.5.1.1: *Type of inks products.*

TYPE	APPLICATION
Process	Printing inks solvent based for flexible packaging
Raster	Printing inks for high definition
Monosolvent	Printing inks for printing from the packaging

As described in *Chapter 3.2*, each production is characterized by a first step of kneading/mixing, a short phase in a grinding mill and a final finishing. Being the grinding mill an isolated device from the surrounding environment, sampling was performed in the ink tank mixture, at the time of the substances load and at the end of the production cycle, that is the finishing process reactor. Therefore, the mixture, in the two situations, has different characteristics in terms of vapor pressure and volatile organic compounds. It has been described a result in the characterization of the three specific prototypes analyzing, in addition to the chemical-physical properties of a gradation for each type of paint, the data necessary for determining the LOC.

4.5.1.1 Gecko process

The line Process Ink constitutes a complete range of high pigmentation concentrated pastes based on nitrocellulose designed to obtain all the Series Gecko in compliance with most of the requests of the market in terms of fastness properties and pigmentation levels. Process Gecko is formed by a wide range of color index; the four-color process is available in a version PROCESS (Ethanol based) and in a retardant version, RASTER, for high definition printing (Ethoxypropanol based).

4.5.1.2 Gecko base monosolvent

The series monosolvent Gecko Base is the central part of the system Gecko, highly versatile and modular, offering flexibility according to the needs of the customer. The series Gecko Base monosolvent consists of a wide range of color index. They include a white and a full color, along with other special color index.

4.5.2 Vapors flammability

Hazards from processes using chemicals are assessed on the basis of:

- Inherent chemical properties Toxic, flammable/explosive, reactive, unstable;
- Chemical form Liquid, solid (briquette, flake, powder), gas, vapour, airborne

particulate (including mist, fume, froth, aerosol, dust);

- Quantity in storage, held up in process stages, in the working atmosphere, as wastes, etc.;
- Processing conditions;
- Use of high or low temperature, high pressure, vacuum.
- Possible hazardous reactions (polymerization, oxidation, halogenation, hydrogenation, alkylation, nitration, etc.).

Hazards can often be foreseen from basic physicochemical principles, as summarized below. Since the processing temperature in the reactors decidedly superior to that environment, what will be analyzed in the present study will be the vapors generated by these inks and not the liquid inks themselves. It is therefore reasonable to consider attributable to volatile solvents the generation of the explosive atmosphere in the surrounding reactors and places of work. Therefore studying the explosivness of the liquid mixture means studying its components in the vapor phase. Following it is studied the behavior of the vapor phase above the free surface of the liquid in contact with the atmospherere whether or not flammable. The solution procedure is divided into the following three steps shown following.

4.5.2.1 Vapor pressure

The vapour pressure of a chemical provides an indication of its volatility at any specific temperature. As an approximation, the vapour pressure P of a pure chemical is given by the Antoine's equation that correlates vapor pressure as a function of temperature as follows:

$$logP = A - [\frac{B}{(T+C)}] \qquad \text{Eq. 4.1}$$

Where:

P vapor pressure, mmHg;
A, B, C Antoine's coefficient;
T °C.

The coefficient tabulation is based on both literature ("Antoine coefficients relate vapor pressure to temperature for almost 700 major organic compounds, C. L. Yaws and H.-C. Yang, Lamar University, Beumont, Texas") and estimated values. Hence the vapour pressure of a chemical increases markedly with temperature. What already said, has been applied to the different tipologies of liquid mixtures and vapor phase composition determined. For simplicity only the BLUE GECKO_RASTER ink has been studied since what really matters is understanding properties connected to hazardous chemicals. However, all calculations have been reported in Annex I., in addition, ink's vapor phase in mixing and finishing reactors have shown equal behaviour, so the same calculations have been adapted to both of them. Antoine's coefficients have been taken from literature and the vapor pressure curve as a function of temperature have been built up. The vapor pressure of a liquid changes with its temperature, as the following Tab. 4.4.2.1.1 and Fig. 4.4.2.1.1 shows for the color already mentioned.

Tab. 4.4.2.1.1: *Singular compounds and mixture's vapor pressure.*

T (°C)	Vapor pressure (Pa)			
	Ethanol*	**Ethyl Acetate***	**EthoxyPropanol***	**Ink**
0	1.589	3.381	296	**927**
10	3.139	5.988	553	**1.814**
20	5.873	10.105	991	**3.370**
30	10.474	16.341	1.710	**5.975**
40	17.900	25.450	2.854	**10.168**
50	29.447	38.340	4.622	**16.676**

60	46.816	56.068	7.280	**26.456**
70	72.177	79.843	11.177	**42.464**

*[Antoine coefficients relate vapor pressure to temperature for almost 700 major organic compounds, C. L. Yaws and H.-C. Yang, Lamar University, Beumont, Texas]

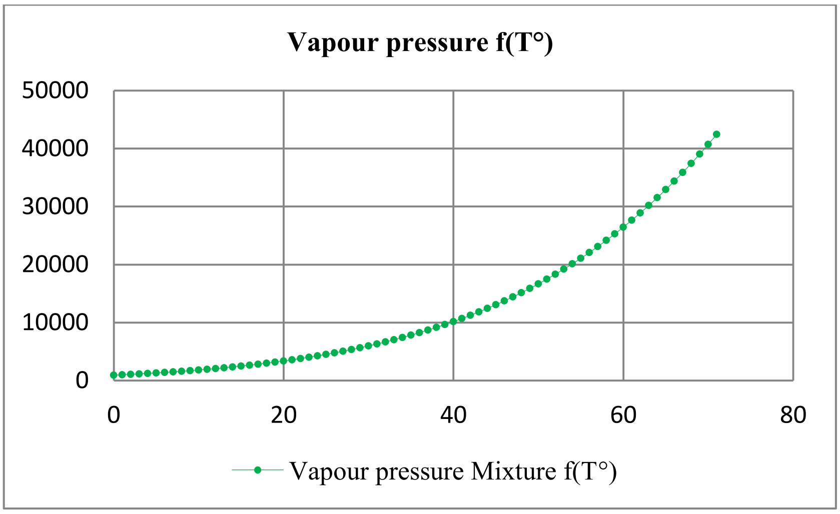


Fig.4.4.2.1.1: *Ink's vapour pressure as a function of temperature.*

4.5.2.2 Dalton's law

For a component 'a' in a mixture of vapors, its partial pressure P_a is the pressure that would be exerted by that component at the same temperature if present alone in the same volumetric concentration. So with a mixture of two components, 'a' and 'b', the total pressure, according to the Dalton's law, is:

$$P = P_a + P_b \qquad \text{Eq. 4.2}$$

If an inert gas is also present, its pressure is additive:

$$P = P_a + P_b + P_{inert} \qquad \text{Eq. 4.3}$$

According to Rault's law, in an 'ideal mixture', the partial pressure P_a is proportional to the mole fraction y_a of the component in the gas phase:

$$P_a = y_a * P \qquad \text{Eq. 4.4}$$

and this partial pressure is also related to the concentration in the liquid phase expressed as mole fraction x_a by:

$$P_a = P_{a*}\, x_a \qquad \text{Eq. 4.5}$$

where P is the vapour pressure of component 'a' at the prevailing temperature. So, if all the components are miscible in the liquid phase the total pressure P of a mixture is:

$$P = P_a\, x_a + P_b\, x_b + P_c\, x_c \qquad \text{Eq. 4.6}$$

As a result:

- The flash point of any flammable liquid will be lowered if it is contaminated with a more
- volatile, flammable liquid;

- Application of heat to a flammable liquid (e.g. due to radiation or flame impingement in a fire, or because of ‘hot work’) can generate a flammable vapor-air mixture;
- The composition of the vapor in equilibrium with a miscible liquid mixture at any temperature, will be enriched by the more volatile components.

Then, applying Dalton’s and Rault’s law at T=10°, the molar and gas phase have been determined as shown in Fig. 4.4.2..1.2:

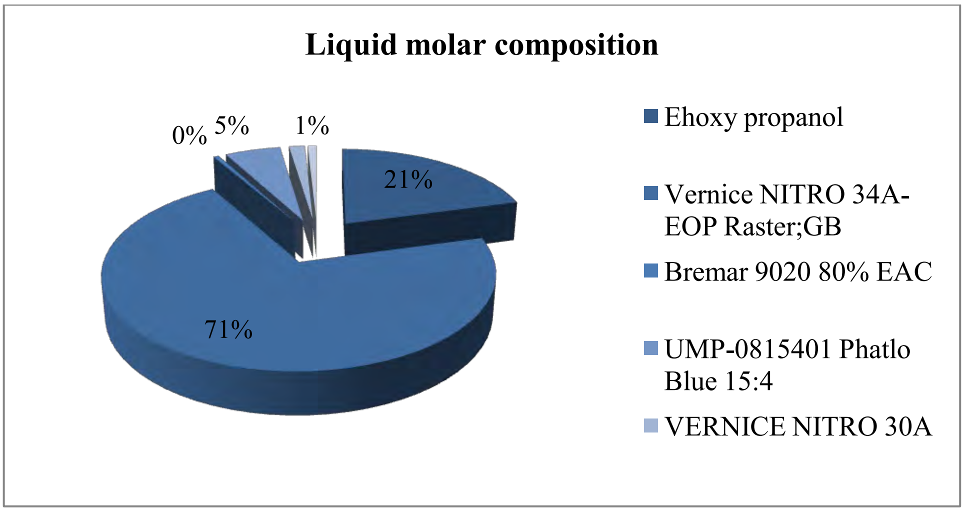


Fig.4.4.2.2.1: *Liquid molar composition of ink.*

Each component of the mixture was analyzed individually, and finally the overall volatile explosives were quantified to determine and study the vapor phase (Fig.4.4.2.1.3) :

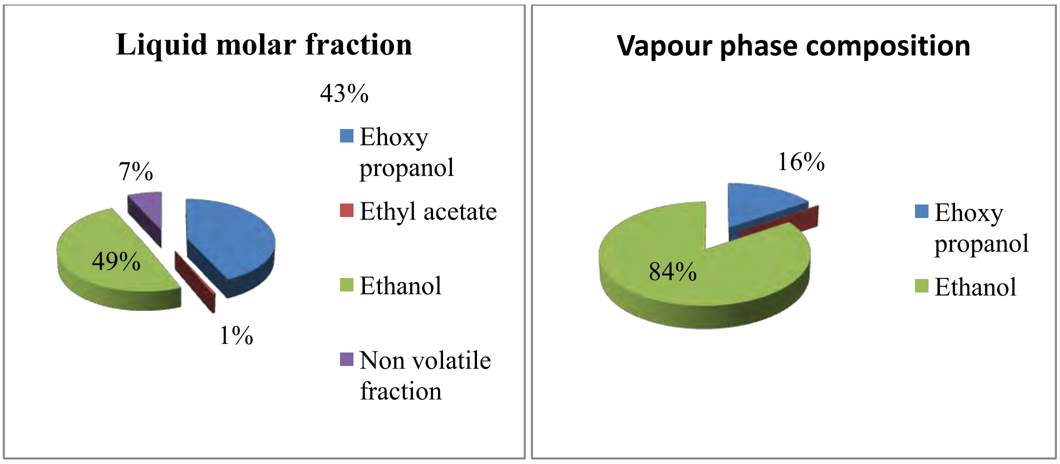


Fig.4.4.2.2.2: *Volatile components of the ink: a) liquid composition; b) vapor composition.*

At this point, some conclusions can be drawn, representing the assumptions of the project. Firstly, it can be noted, from Fig. 4.4.2.2.2, that 84% of the vapor phase of the mixture consists of ethanol and the remaining 16% of ethoxypropanol; furthermore, by comparing the vapor pressures, Tab. 4.4.2.2.1, it can be noticed the greater volatility of ethanol with respect to ethoxypropanol. It has been, therefore, decided to assume, in favor of safety, that the vapor phase is 100% ethanol gas. In fact, comparing the vapor pressures of ethanol and mixture, establishing this assumption means attributing to the mixture a higher volatility with respect to the real one, thus acting in favor of safety. This also allows the use of tabulated data and thus more reliable and real than those ones obtained theoretically.

4.5.3 Flammability identification

Flammable gases and volatile liquids are particularly hazardous because of the relative ease with which they produce mixtures with air within the flammable range. An increase in the surface area of any liquid facilitates vaporization. For each substance there is a minimum concentration of gas or vapour below which flame propagation will not occur (i.e. the mixture is too lean). There is also a concentration above which the mixture is too rich to ignite. Starting with basic definitions, the lower and upper flammability (or explosibility) limits (LFL and UFL, respectively) are the limiting fuel concentrations in air that can support flame propagation and lead to an explosion. Fuel concentrations outside those limits are non-flammable. The limits of flammability are influenced by temperature and pressure (e.g. the flammable range expands with increased temperature. Recalling the theory of combustion for previously discussed, it shows the flammability characteristics of the mixture under examination:

Tab. 4.5.3.1: *Flammability iidentification of the ink.*

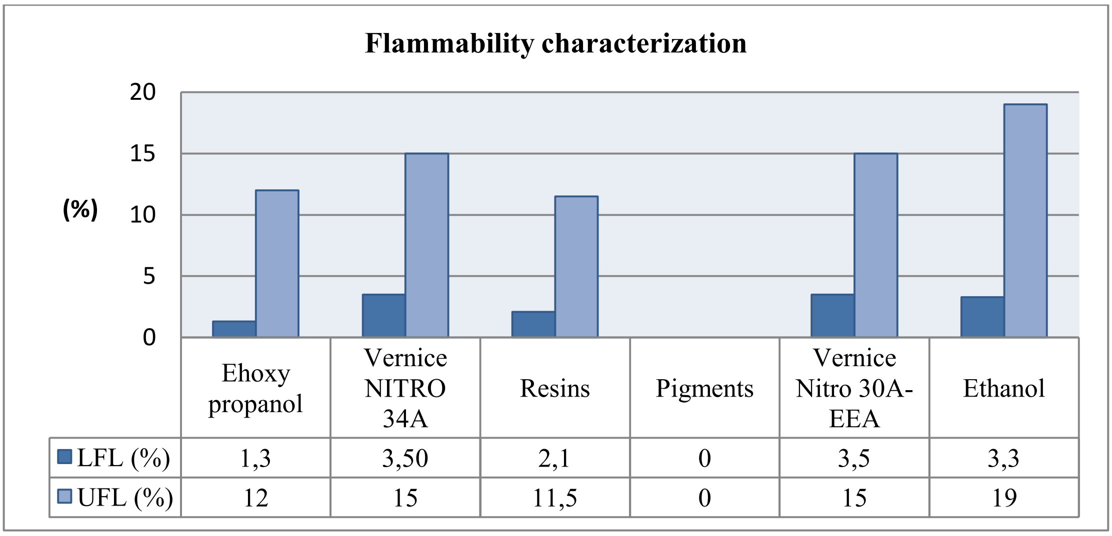
Flash point	**20**	**°C**
Autoignition Temperature	425	°C
LFL	3,3	%
UFL	19	%
Vapor pressure	3.370	Pa

The previous Tab. 4.4.3.1 reports LEL and UEL at T=20° determined experimentally and other physical parameters necessary for flammability characterization. In performing the flammability tests were taken from the following legislation, previously reported:

I. UNI EN 1839 (LEL and UEL for gases and vapors);
II. UNI EN 14034-3 (LEL for combustible dusts).

Analyzing the individual components of the mixture, it is shown in the following Tab. 4.5.3.2:

Tab. 4.5.3.2: *Flammability limits of ink's components*.



	Ehoxy propanol	Vernice NITRO 34A	Resins	Pigments	Vernice Nitro 30A-EEA	Ethanol
■ LFL (%)	1,3	3,50	2,1	0	3,5	3,3
□ UFL (%)	12	15	11,5	0	15	19

Some empirical equations used to correlate the explosion limits to the temperature ("*Zabetakis, 1965; Crowl et al., 2002"*):

$$LEL = LEL_{20} - \frac{0{,}75}{\Delta H_C}(T - 20)$$ Eq. 4.7

$UEL = UEL_{20} - \frac{0{,}75}{\Delta H_C}(T - 20)$ Eq. 4.8

Where:
ΔH_C is the net heat of combustion (kcal/mol);
T Temperature (°C), the subscript 25 indicates the reference to the ambient temperature.

The pressure influences the field of explosion, with the modification UEL, according to the following relationship:
$UEL_P = UEL + 20{,}6 \cdot (LogP + 1)$ Eq. 4.9

Where:
P pressure (absolute MPa).

Curves of flammability limits as a function of temperature and pressure has been built up as shown in Fig. 4.5.3.1. The temperature greatly influences the characteristics of flammability, as it acts on the vapor pressure, on the reaction rate, limits of flammability, on the speed of flame propagation, the tendency to self-ignition, etc. Usually, a temperature increase produces a widening of the interval of flammability, that the lower limit is lowered while the top is raised. The limits vary linearly with the temperature and the effect is felt mainly on the upper limit.

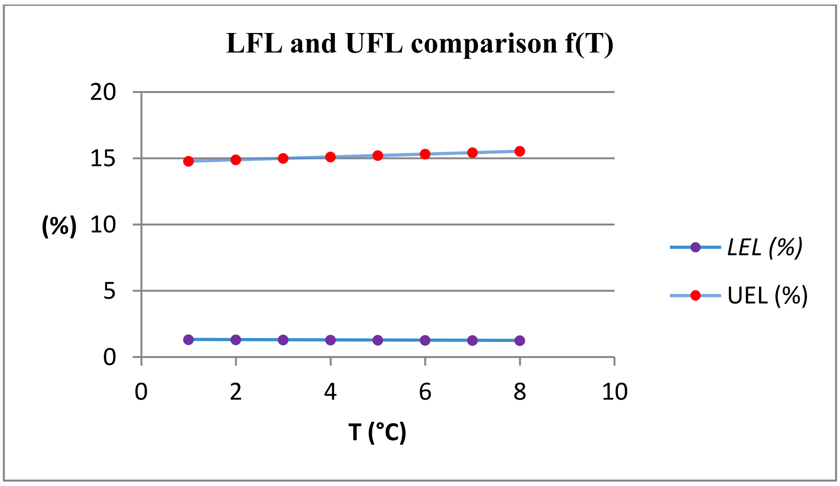


Fig. 4.5.3.1: *LFL and UFL as a function of Temperature.*

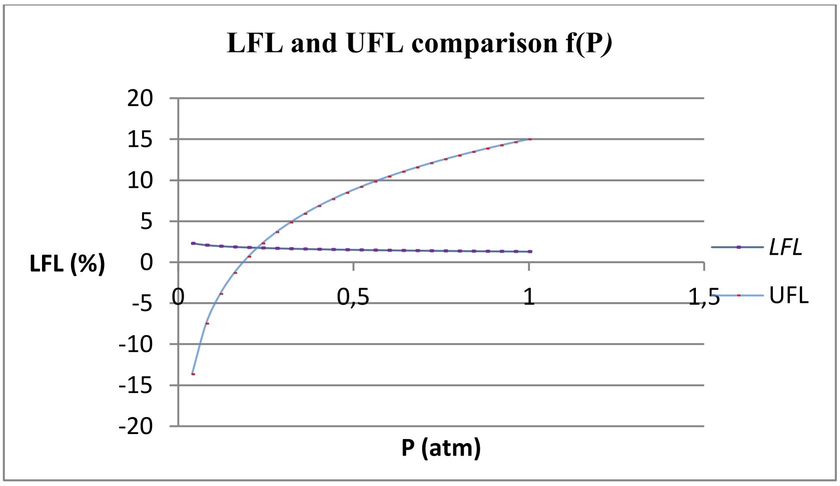


Fig. 4..3.2 : *LFL and UFL as a function of Pressure.*

Also the pressure influences the reaction rate, the speed of propagation of the flame and the limits of flammability. In general, higher pressures tend to widen the range of flammability, lower pressure to narrow it. By reducing the pressure, the flammability limits approach each other: at a very low pressure level, flame spread can be prevented so that the mixture becomes not explosive (meaning negative numbers %). Increasing the pressure, instead, the range of flammability extends, particularly as a consequence of increasing the upper limit. In practice, however, the effect of pressure on the limits of flammability is not always easily predictable, since it is not always exerts the same direction but and very specific situation of each mixture. The percentage achieved by the vapors of the mixture in the air is as follows (Tab. 4.5.3.3):

$$V\ (\%) = \frac{P_{sat}}{P} \cdot 100 \qquad \text{Eq. 4.10}$$

Tab. 4.5.3.3*: Percentage of volume in air of vapor mixture.*

	T = 10°	**T = 40°**	**T = 65°**
Vapour Pressure	3.200 Pa	17.900 Pa	58.342 Pa
V (%) in air	3,4 %	18 %	57 %
LFL	3,3 %	3,25 %	3,2 %
UFL	18,9 %	19,3 %	19,6 %

As it is possible to observe from the Tab. 4.4.2.1.1, at the operating temperatures of 40° and 10°, the % of vapors of the mixture falls in the flammability zone defined by the Lower Flammability Limit and the Upper Flammability Limit. The progressive additions of an inert gas to a fuel-air mixture causes the narrowing of the flammability range to the point where the two limits coincide.

4.5.4 Limiting Oxygen Concentration

The limiting oxygen concentration (LOC) is the minimum O_2 concentration in a mixture of fuel in air that will propagate flame. The individual component to the vapor phase, was calculated stoichiometric oxygen for complete combustion, whereas the following stoichiometry:

$$C_2H_5OH + 3O_2 \longrightarrow 3H_2O + 2CO_2$$

Tab. 4.5.4.1: *Moles of oxygen request for complete combustion of ethanol vapor.*

	Vapor phase (%v/v)	**Mol of O_2/mol of compound**	**Mol of O_2 request**
Ethanol	100	3	3

According to the method proposed by Crowl and Louvar (Crowl et al., 2002), it is, therefore, been calculated the total amount in terms of moles of oxygen, determining the LOC of the mixture according to the formula:

$$LOC = \frac{Lower\ explosion\ limit * Stoichiometric\ moles\ of\ oxygen}{Stoichiometric\ moles\ of\ gas} \qquad \text{Eq. 4.11}$$

In the case of ATEX mixtures, composed of more flammable substances, the overall LEL and UEL is determined with the aid of the Le Chatelier's law:

$$LFL = \frac{1}{\sum \frac{Xi}{LFLi}} \qquad \text{Eq. 4.12}$$

Where Xi is the mole fraction or volume of the ith substance. According to Eq. 4.12, thus assuming 100% Ethanol and on the basis of Eq. 4.11, LOC value has been calculated:

$$LOC = \frac{LEL * moles\ of\ Oxygen}{moles\ of\ Ethanol} = \frac{3{,}3 * 3}{1} = 9{,}9\%$$

It's easily understandable that the mixture in contact with air is flammable, since air oxygen composition is 21%. The European Printing Inks Association, to which reference is made in this study, recommend strongly to maintain an inert atmosphere in tanks containing flammable hazardous liquids, ensuring a minimum oxygen concentration below 8%; this guideline has been issued by the European Printing Inks Association (EUPIA) on september 2007- replaces the july 2004 edition - for all industries handling flammable liquids in coatings and printing inks manufacturing sites, as raw materials, finished products or others.

Tab. 4.5.4.1: *Limiting Oxygen Concentration: theoretical and experimental calculation.*

	Stoichiometric moles of O_2	***LFL (%)***	***LOC (%)***
T = 20°	3	3,3	9,9 %
T = 45°	3	3,25	9,51 %
T = 65°	3	3,2	9,75 %

The lower accuracy attributable to the results obtained at T = 45 °C and T= 65 °C is connected to the fact that the LFL were obtained by a theoretical interpolation (*Eq. 4.7 and 4.8*), while the result is an experimental data. That rule is less adequate, still generally conservative in predicting the UFL of mixtures, but unfortunately it is not of interest this parameter.

Chapter 5. Alternative solution – Tanks blanketing

Preventing the formation of ATEX in workplaces imposes specific obligation in place head to the Employer. In this sense, the art.289, paragraph 1 of Legislative Decree. N. 81/2008 is particularly explicit, reciting:

> "*For the purpose of prevention and explosion protection, based on an assessment of risks and the general principles of protection under Article. 15, Leg. n. 81/2008, the employer shall take technical and organizational measures to the nature of the business: in particular, the employer prevents the formation of explosive atmospheres.* "

Strategies aimed at preventing the formation of potential ATEX consist mainly of technical solutions:

- Adoption of a general ventilation with the following characteristics: HIGH degree of ventilation and GOOD availability;
- Containment or vacuum dust with GOOD availability;
- GOOD level of maintaining or cleaning of dust layers;
- HIGH (or MEDIA) Local exhaust or degree of effectiveness and GOOD availability;
- Minimization of the emissions through the adoption of high efficiency seals (eg. spiro metal in place of the compressed fiber);
- Maintenance of facilities aimed at the minimization of releases;
- Adoption of explosion control system which limit the classification of the far field;
- Inerting gas;
- Concentration of flammable mixture outside the explosion range LEL-UEL;
- Substitution or reduction of the amount of substances capable of forming ATEX (dilution of flammable with water, the presence of sufficient moisture in powders).

As discussed in *Chapter 3*, the prevention of the formation of ATEX in production areas, is actually implemented through local exhaust with HIGH degree of effectiveness; however, as estimated in the fire risk assessment, *Chapter 4*, this measure is not yet sufficient to obtain an acceptable residual risk. It is therefore proposed, following, the study of the inertization technique as a preventative measure, alternative to the current one, in order to reduce the residual risk to a more acceptable value. Particular reference is made to NFPA 69 (National Fire Protection Association, 1997), Standard on Explosion Prevention Systems: this standard provides requirements for installing systems for the prevention and control of explosions in enclosures that contain flammable concentrations of flammable gases, vapors, mists, dusts, or hybrid mixtures.

5.1 Inertization

As already mentioned, the Title XI ("protection from explosive atmospheres") of Legislative Decree no. 81/2008 lists the various measures that companies need to take to assess and prevent risks from explosive atmospheres, where "explosive atmosphere" means mixtures with air at atmospheric conditions, of flammable substances in the form of gases, vapors, mists or dusts in which, after ignition, combustion spreads throughout the unburnt mixture. The flammability diagram, presented in the following *Section 5.2,* provides target gas concentrations to avoid the flammability zone. Inerting and purging procedures are used to achieve that concentration. The inerting is the main strategy to prevent the formation of explosive mixtures inside the containment process. It consists in adding an inert gas to the point to which is reached an oxygen concentration such as to allow the closure of the explosion range (LEL-UEL). This concentration of oxygen is defined LOC (defined and determined in *Chapter 4.4.4*) and is a function of the inert gas used

(Tab 5.1.1). The power of the inerting gas is a function of the chemical species used and decreases in the following order:

1. Carbon dioxide;
2. Water vapour;
3. Exhaust gases produced by motors;
4. Nitrogen;
5. Argon or helium.

Not all inert gases are, however, usable in industrial systems. In particular, the water vapor and the carbon dioxide can react with the light-metal dusts (eg. Aluminum, magnesium, titanium) while nitrogen promotes exothermic reactions at high temperature with powders of magnesium. The effectiveness inerting of the water vapor, also, is strongly conditioned by the presence of cold walls on which the vapor condenses; this phenomenon can occur especially during startup of process plants not preheated. The carbon dioxide, finally, promotes the generation of electrostatic charges that can provoke serious risks of ignition in cases where the mixture is not completely inert. Tab. 5.1.1 shows the main advantages and disadvantages of using the most common inerting gas.

Tab. 5.1.1: *Advantages and disadvantages of most common inerting gas.*

Gas	Advantages	Disadvantages
Carbon dioxide	It is available in the form of compressed gas cylinders or through the recovery of exhaust gases of the process. The actual percentages of oxygen are allowed higher than required using nitrogen. It has a moderate cost (almost nil if produced by the process).	Some metals may react violently (Al, Mg). The CO_2 stream may generate a considerable accumulation of electrostatic charges.
Water vapour	It can be generated by technological processes in the system.	It may not be available during the phases of start and stop of the plant. The water vapor is incompatible with many combustible dusts. Condensation can disable the neutralizing process.
Exhaust gas	Usually available as exhaust of the combustion process. Very modest cost.	It is necessary to install heat exchangers, scrubbers, sensors that detect the presence of flammable vapors, sensors that intercept any hot coals. Prò react with some dust. The storage is not practiced so that the availability of the gas is linked to the operation of the process that generates the exhaust gas.
Nitrogen	It is available in the form of cryogenic gas compressed and, in some cases, as a waste product of the process.	It is less effective, in terms of concentration, compared to carbon dioxide. It reacts at high temperatures with the magnesium.
Argon and Helium	They do not contaminate the products and does not react with them.	Very expensive.

Of course the choice of the inert gas should be realized considering some factors including:

- Efficacy or inerting gas;
- Possibility of storage;
- Ability to supply;
- Cost of gas;
- Process conditions;
- Risks related to the safety of workers.

Anyway, inerting techniques exist for a great variety of tasks as list following:

Purging usually refers to the process of changing the gas concentration within a vessel or process, usually with either an inert gas (to decrease the oxygen concentration) or a fuel gas (to increase the fuel concentration). Inerting usually applies to maintaining an inert gas blanket in a vessel or process. The two terms are frequently used interchangeably.
Blanketing, or *padding*, is the technique of continuously maintaining an atmosphere that is either inert or fuel rich in the vapor space of a container or vessel**.** An inert gas is admitted to an apparatus or pipeline in order to displace a process gas from it. The operation is monitored through the flow rate and pressure of the inert-gas stream and/or the oxygen level in the gas exiting the vessel.

Sparging means passing finely dispersed gas through a liquid in the form of bubbles in order to improve mixing and to increase the surface area for gas-liquid mass transfer. The technique finds use in chemical and biological reactions and also in stripping. Purging and blanketing process vessels and equipment are two common, yet distinctive, practises to control the concentrationof oxygen, thereby reducing fire and explosion hazards.

Fig. 5.1.1: *Example of inertized process reactors.*

Blanketing helps protect plant personnel, products, and plant assets by reducing the oxygen content in the vapor space of a storage tank or process vessel, making it inert. This eliminates the possibility of fire or explosion, decreases evaporation, and protects the tank from structural corrosion damage caused by air and moisture. It also prevents air, moisture, or other contaminants from entering the vapor space and causing product degradation. It provides flammable products from coming into contact with the oxygen in air, thereby creating a nonflammable environment that prevents fire and explosion.

5.2 Flammability range of the mixture

As it is known, so that a gas or a vapor infiammabile or a combustible powder mixed in air, give rise to an explosion, it is necessary that the following conditions occur simultaneously:

- The flammable substance is on the air in the field of explodibility (Flash);
- There is any source of ignition effective (eg. Source of mechanical, electrical, electrostatic).

The ignition energy of the majority of flammable gases and vapors is very low, in the order of 0.2 MJ, while in the powders ranges (depending on the material and particle size) between 1 and 10 mJ. It is therefore clear that , in particular, in the presence of flammable gases or vapors, it is very difficult to exclude a priori any possible cause of ignition and should therefore act on the first of the two elements; what it is required to ensure that the substance is not flammable is never mixed in the air within the explosion limits. The elimination of ignition sources is not sufficient to prevent fires and explosions, the ignition energies are too low and ignition sources too plentiful to use this as the primary prevention mechanism. A more robust design alternative is to prevent the existance of flammable mixtures as the primary control, followed by the elimination of ignition sources as the secondary control. The flammability diagram is an important tool for determining if a flammable mixture exists, and to provide target concentrations for inerting and purging procedures presented in *Section 5.5*. The explosion range of a flammable substance mixed with the air is less and less extensive than that of the same with the only flammable oxygen, as the nitrogen present in the air (about 79%) does not react chemically in the combustion and is therefore to consider a diluent which reduces the flammability of the mixture. The presence of inert gases (N_2, CO_2, etc.) substantially lowers the upper explosion limit of the fuel, without varying significantly lower. The flammability triangle (Fig. 5.2.1) describes this connection in order to represent the behavior of mixtures fuel/oxidant/inert.

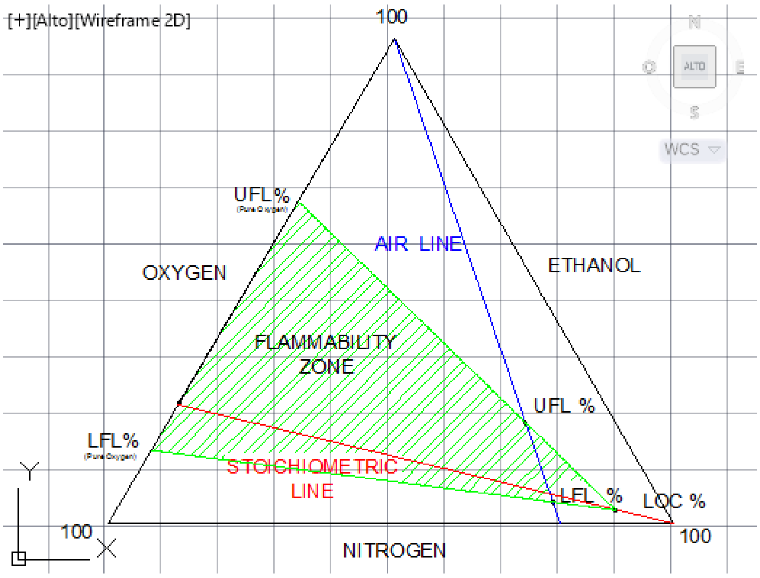


Fig. 5.2.1: *Fire triangle.*

The axis of the diagram represent the concentrations of each of the three components - fuel, oxygen and nitrogen. At any point on the figure, the concentrations must add up to 100%; most flammable materials demonstrate a flammability zone (the shaded area in figure 5.2.1) where the mixture is flammable at all concentrations. The blue line represents the air line. This line runs from point at the top of the triangle (i.e. 100%) to the point on the diagram that corresponds to a concentration of 79% nitrogen and 21% oxygen (i..e., pure air) and represents all possible concentrations of a fuel and air mixture. The red one represents the stoichiometric line. This line runs from the point on the diagram corresponding to a concentration of 100% nitrogen to the oxygen axis and represents all possible stoichiometric concentrations of a fuel and oxygen mixture. The point at which the stoichiometric line intersects oxygen axis depends on the stoichiometry of the general reaction:

$$C_mH_xO_y + zO_2 \longrightarrow mCO_2 + (x/2)\,H_2O$$

For this reaction the stoichiometric line intersects the oxygen axis at:

$$100 * \left(\frac{z}{1+z}\right)$$

The air line intersects the flammability zone at the flammability limits (i.e., LFL and UFL). The LOC is found at the point where a line parallel to the fuel axis just touches the flammability zone; its value is read from the oxygen axis. Triangle flammability diagrams is useful to determine wheter the flammable mixture will form during normal operation. The hatched area bounded by the air line and stoichiometric line is all the points that correspond to mixtures whose composition allows the spread of flame; outside, all the points correspond to non-flammable mixtures. The pressure and temperature have an effect on the flammability diagram similar to the dependence of the flammable limits; an increase in temperature causes a decrease of the LEL% and a consequent reduction of the LOC. In the previous section, instead, it has shown the increase of the LOC increasing temperature. On the other hand, an increase in temperature causes an increase of the UEL% that altogether amplifies the field of flammability of the mixture.

In contrast to this, however, the dosage of inert gases (N_2, CO_2, etc.) affects the Limiting Oxygen Concentratiom, substantially lowers the upper flammability limit of the fuel, without varying significantly the lower one. In this way the flammable range narrows; the progressive addition ends until the two limits practically coincide, inertizing the mixture. Figure 5.2.2 shows the procedure for placing the vessel into service. The vessel begins with air, shown as point A. Nitrogen is pumped into the tank until point S is reached. Then fuel is pumped in, following line SR until point R is reached. Point S starting values are shown in Tab 5.2.1. A wider analysis of how to determine this value will be discussed in Chapter 5.11. The in-service oxygen concentration (ISOC) represents the maximum oxygen concentration at point S on Figure 5.2.2 that just avoids the flammability zone. From a practical stand point, an oxygen concentration some what less than the values would be desired to ensure that the concentrations stay well away from the flammability zone.

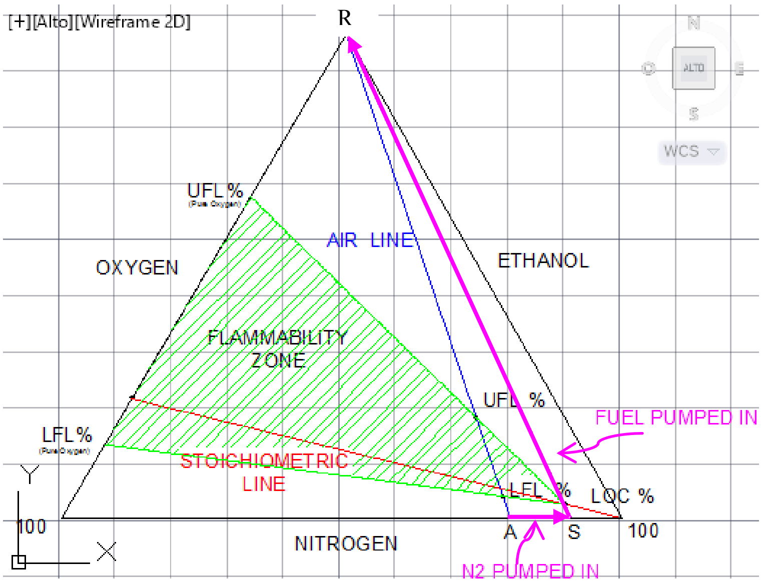


Fig. 5.2.2 : *A procedure for avoiding the flammability zone for placing the process reactor into service.*

According to Chapter 4.4.4, The LOC value of ethanol vapors in air is 9,9%, which lies between the LOC obtainable with the addition of nitrogen and that one obtained with the addition of carbon (Tab. 5.2.1).

Tab. 5.2.1: Ethanol *LOC values according to addition of inert gas.(NFPA 69)*

LOC	
Nitrogen	9 %
Carbon dioxide	11,0 %

Care must be taken to ensure that the flammability zone for all operations is avoided by an appropriate safety margin. NFPA 69 (1997) requires a target oxygen concentration for storage vessels of at least 2% below the measured LOC, if the oxygen concentration is continually monitored. If the LOC is less than 5%, the target oxygen concentration is no more than 60% of the LOC. If the oxygen concentration is not continuously monitored, then the equipment must not operate at more than 60% of the LOC, or 40% of the LOC if the LOC is below 5%.

5.3 Type of vessels

When considering a new blanketing design or an upgrade of an existing installation, the first factor to consider is the type of vessel. Vessels are of two types:

- Fixed roof tank (Fig. 5.3.1 a));
- Floating roof tank (Fig. 5.3.1.b)).

In this case, the inertization will be carried out on existing tanks, using cover and then carry out pressurization. The ones of interest are of fixed roof type. When flammable or sensitive materials are stored in fixed-roof tank, blanketing infact is highly recommended. Floating-roof tanks usually are not blanketed because there is no headspace where vapor could buid up. The headspace above in the internal roof of a covered floating-roof tank (or internal-floating-roof tank) is occasionally blanketed. It is commonly used to store large quantities of petroleum products such as crude oil or condensate.

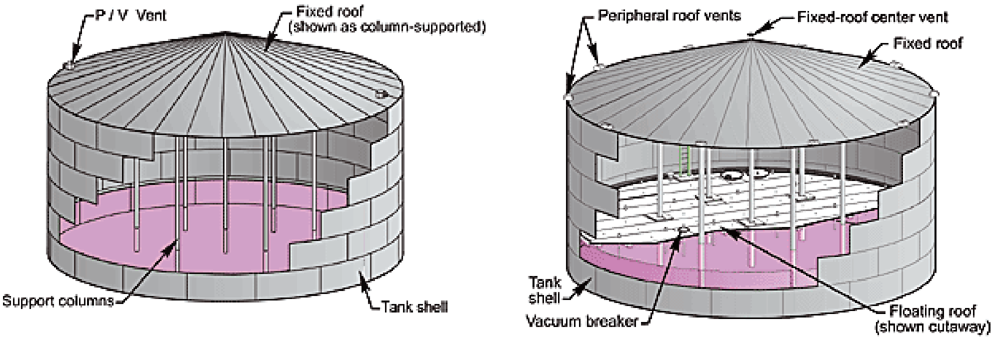


Fig. 5.3.1: *a) Fixed and b) floating roof tanks*.

5.4 Possible systems configurations

The objective of the system of distribution of the inert gas is to ensure that oxygen is always maintained below the LOC in all zones of the protected facility. *NFPA 69* provides a detailed approach to the problem of supply, distribution and monitoring of inert gas. To impurities such as rust and moisture it must not be allowed to enter the plant to be protected; It is for this reason that the gas is filtered in such a way as to minimize the rate of dust and moisture transported. The system must also be equipped with non-return valves which prevent gas contamination caused by possible lowerings of pressure in the pressure line, or pressure in the vessel to be protected. This precaution is necessary in particular if there are many points of introduction of inert gas in the plant. It must also be kept under control the excessive flow of gas due to valves and control devices of the pressure continuously. In the case of recycling of inert gas, particular attention should be paid to the capture of combustible dust in it transported through a fabric filter systems (sub-sleeved). There are essentially two power supply systems (inert gas):

- A fixed power ratio (Fig. 5.4.1): the advantages of this system are the extreme simplicity of the plant (in fact installed are not sophisticated and expensive devices such as pressure regulators) and the low cost of maintenance while the main disadvantage consists in the excessive amount of nitrogen used;
- A variable-rate-purging (Fig. 5.4.2): this system is commonly used and regulates the supply of inert gas to the fluctuation of demand. The advantages of this system consist in the feeding of inert gas only when

requested by acting, for example in the case of discharge of material (decrease of pressure in the container), increasing the flow of inert gas inlet. The disadvantages are due to the malfunctioning of control valves differential that may not work at times, under conditions of low pressure differential. In general, due to high volumes of inert gas involved, the inertization process can be realized only in installations confined or semiconfined, which may be only an exchange of gaseous volume reduced unit time.

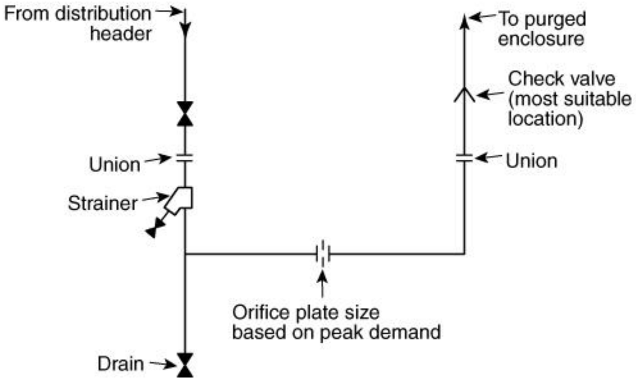


Fig. 5.4.1: *Method of flow control for Use with Fixed-Rate Purging.*

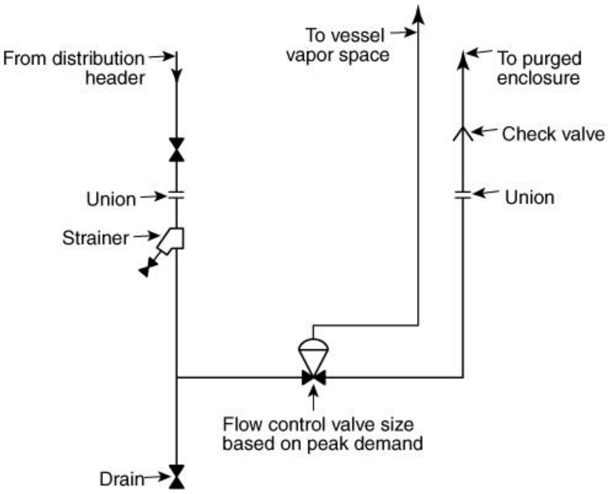


Fig. 5.4.2: *Method of flow control for Use with Variable-Rate Purging.*

5.5 Purging methods

5.5.1 Siphon Purging

In this method, equipment might be purged by filling with liquid and introducing purge gas into the vapor space to replace the liquid as it is drained from the enclosure. The volume of purge gas required is equal to the volume of the vessel, and the rate of application can be made to correspond to the rate of draining.

5.5.2 Pressure purging

The pressure purging is a particularly efficient system of inerting. It is normally used in the recipient process able to withstand overpressures (sometimes also relevant). In this method, enclosures might be inerted by increasing the pressure within the enclosure by introducing purge gas under pressure and, after the gas has diffused, venting the enclosure to the atmosphere. More then one pressure cycle might be necessary to reduce the oxidant content to desired percentage.

The concentration of oxygen decreases with the increasing number of cycles of purging until reaching the value of security provided for the process. Particular attention should be paid to the maximum purging pressure; it must always be lower than the calibration pressure of the rupture discs or safety valves are installed on the reactor. The concentration after n purging cycles, assuming an isothermal compression, is the following:

$$C_n = C_i + (C_0 - C_i) \cdot \left(\frac{P_{min}}{P_{max}}\right)^n \qquad \text{Eq. 5.1}$$

Where:

C_n is the oxygen concentration after n purging cycles;

C_i is the oxygen concentration in the inert gas;

C_0 is the initial oxygen concentration;

P_{min} is the minimum pressure of the cycle;

P_{max} is the maximum pressure of the cycle;

n is the number of purging cycles.

In the case where the oxygen concentration in the inert gas is negligible, the equation simplifies to the following:

$$C_n = C_0 \cdot \left(\frac{P_{min}}{P_{max}}\right)^n \qquad \text{Eq. 5.2}$$

If the maximum pressure of the cycle are relevant or are present rapid changes in pressure, the process can no longer be considered isothermal but adiabatic and the cycles will be calculated as follows:

$$C_n = C_i + (C_0 - C_i) \cdot \left(\frac{P_{min}}{P_{max}}\right)^{\frac{n}{k}} \qquad \text{Eq. 5.3}$$

Where:

k is the ratio of specific heats at constant pressure and volume.

A particular form of the above equations, provided by Barton also introduces the value of mixing efficiency M. There is, then:

$$n = \frac{ln\left(\frac{C_n}{C_0}\right)}{ln\left(\frac{P_{min}}{P_{max}}\right)} \cdot \frac{1}{M} \cdot k \qquad \text{Eq. 5.4}$$

Where two or more containers or tanks are joined by manifold and should be purged as a group, the vapor content of each container or tank should be checked to determine that the desired purging has been accomplished. Where a container filled with combustible material is to be emptied and then inerted, purge gas might be applied to the vapor space at a pressure consistent with equipment design limitations, thus accomplishing both the emptying of the vessel and the purging of the vapor space in the same process. In the hypothesis in which there are systems of direct monitoring of the percentage of oxygen inside the containment, it will be unnecessary to perform checks of the indirect type according to the following procesura valid for reactors in positive pressure:

- Check that the containment, the rupture disc and the safety valves are compatible with the overpressure to be created;
- Close the bottom valve, the hatch and manual valves vent;
- Pressurize the reactor up to the required pressure;

- Wait for at least 5 to 15 minutes making sure that the pressure does not drop;
- If the reactor does not hold pressure it can be due to the rupture disc can be broken, or the hatch is not properly tightened or valves have failed. In this case, stop the operation and notify the person in charge who will intervene to maintenance personnel. Do not carry the load;
- If the pressure holds, vent up by opening the manual valve till to bring to zero the pressure gauge;
- Repeat the n. times required by the procedure;
- Proceed to load the flammable substance.

5.5.3 Vacuum swing purging

The vacuum purging is used only in containers able to withstand variations of negative pressure, connected to one or more groups of vacuum. In this method, equipment that normally operates at reduced pressure, or in which it is practical to develop reduced pressure, might be inerted during shut down by breaking the vacuum with purge gas. If the initial pressure is not low enough to ensure the desired low oxidant concentration, it might be necessary to re-evacuate and repeat the process. The cycle, repeated several times allows to reach with a few cycles the oxygen level of security. The amount of inert gas required is determined by the number of applications required to develop the desired oxidant concentration. Where two or more containers or tanks are joined by a manifold and should be purged as a group, the vapor content of each tank should be checked to determine that complete inerting has been accomplished. The equations governing the process are the same as the ones described for pressure purging with the specification that, being the vacuum process relatively slow, it can be excluded the presence of adiabatic transformations. The main advantage of vacuum purging compared to that in pressure is the savings in the use of inert gas. In view of this important positive aspect, the vacuum process occurs during cycle much more, being much more rapid pressurization of the creation of the vacuum in a container. Both vacuum and pressure purging are particularly critical in the conditions of maintaining inerting in the presence of the following conditions:

- Containment or vented into the atmosphere. The presence of faults in the vent valves may jeopardize the proper generation of an inert atmosphere;
- or introduction of liquids and gases in the containment. Operations of this type, as a rule, do not compromise inerting, if the input of substances is sealed to the atmosphere;
- Introduction of solids in containment. This operation, unlike the previous one, always involves the contact with the atmosphere, unless not to use load box also inertized. If uploads hatch will be essential to provide a flushing interior coupled with an effective local exhaust outside the opening;
- Emptying of the containment. The emptying of the containment will always be made by compensating with inert gas the volume output from the reactor bottom. During vacuum purging, if there are no systems of direct monitoring of the percentage of oxygen inside the containment, it will be unnecessary to perform checks of the indirect type by following, for example, the following procedure (valid for reactors negative pressure):
- Check that the containment, the rupture disc and the safety valves are compatible with the vacuum to be created;
- Close the bottom valve, the hatch and manual vent valves;
- Put the reactor or vacuum up the necessary pressure;
- Close the vacuum valve and wait for at least 5-15 minutes and found that depression does not drop;
- If the reactor does not maintain the vacuum can be broken rupture disc, the hatch is not properly tightened or valves have failed. In this case stop and tell your manager that will intervene to maintenance personnel. Do not carry the expected load;
- If the vacuum is maintained, vented with nitrogen at low pressure until bringing to zero the pressure gauge;

- Repeat as many times as required by the procedure;
- Proceed to load the flammable substance.

5.5.4 Sweep-Through purging

In the case in which the containment is not able to guarantee an adequate resistance to vacuum or to pressure, as in the case of tanks of flammable, it is possible to use the methodology of flushing with inert gas. This method involves introducing a purge gas into the equipment at one opening and letting the enclosure content escape to the atmosphere through an other opening, thus sweeping out residual vapor. The quantity of purge gas required depend on the physical arrangement. A pipeline can be effectively purged with only a little more than one volume of purge gas if the gas can be introduced at one end and the mixture can be released at the other. However, vessels require quantities of inert gas much in excess of their volume. If the system is complex, involving side branches through which circulation cannot be established, the sweep-through inerting method might be impractical, and pressure or vacuum purging might be more appropriate. Assuming that within the system to be inerted is present a perfect mixing between air and the inert gas, it is possible to calculate the duration of the flushing through the following equation:

$$t = f \cdot \frac{V}{Q} \cdot ln\left(\frac{C_i - C_0}{C_i - C_f}\right) \qquad \text{Eq. 5.5}$$

Where:

t time required for inerting;
f factor of efficiency of the ventilation variable from 2 to 5;
V volume of the system;
Q flow rate of inert gas;
C_f oxygen content after the flushing;
C_o initial concentration of oxygen;
C_i content of oxygen in the inert gas.

In the case where the content of oxygen in the inert gas is negligible, the above equation is reduced to the following:

$$t = f \cdot \frac{V}{Q} \cdot ln\left(\frac{C_0}{C_f}\right) \qquad \text{Eq. 5.6}$$

The relationship between the number of volumes of purge gas circulated and the reduction in concentration of the critical component in original tank contents, assuming complete mixing, is shown on the graph in Fig. 5.5.4.1.

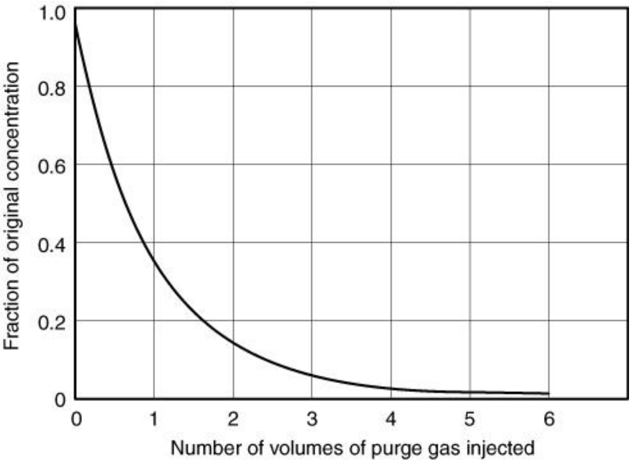


Fig. 5.5.4.1: *Dilution Ratio – Purging at atmospheric pressure.*

It should be noted that the total quantity required might be less than that for a series of steps of pressure purging; moreover, four to five volumes of purge gas are sufficient to almost completely displace the original mixture, assuming completely mixing.

5.5.5 Criteria for the selection of proper solution

The method of *Inerting* chosen will depend upon several factors, as follows:

1. The process itself, continuous or batch (or simple storage);
2. The design pressure of the equipment, i.e. its suitability to withstand pressure
or vacuum;
3. The financial implications of the various types of *Inerting*: demand, price, type of generation, constant flow or intermittent flow, etc. ;
4. Health and ecological considerations.

In addition, there are several different types of inert gases available, as seen previously, for instance carbon dioxide and nitrogen, which are the usual gases, but also on-site exothermic gas generators, endothermic gas generators, noble gases, steam and flue gases from boilers, furnaces etc. They all have different characteristics, but the choice of inert gas is usually led by (a) availability of supply, and (b) costs. It is usual to use nitrogen, but it must be realised it is not the only gas available, and others may be more obscure, but, for given functions, may be more desirable. The purpose of the choice of inert gas is to satisfactorily ensure that the concentration of oxygen in the atmosphere never reaches the level at which an explosion can be supported. In order to ensure this aim is achieved, the Inerting system must be appropriately designed.

5.6 Reliability of the system of monitoring and control

The security of the entire strategist prevention ot the ATEX atmosphere through inerting is based on the reliability of monitoring systems, where they are provided. A system of monitoring and control is essential to establish and maintain the safety conditions achievable with inerting. The reliability of this system is therefore essential to reduce the risk from explosive atmospheres. The reliability of the system of monitoring and control must be ensured with the application of the technical standards of the series IEC 61508 and IEC 61511 [CEN / TR 15281, art. 8]. Three methods are commonly used for inert gas control:

- Continuos purge;
- Inferential methods;
- Oxygen concentration control.

Continuos purge systems employ a constant flow of nitrogen. This approach, while sample, has several disadvantages. First, its inert gas consumption rate is high. In addition, the flowing gas may strip the vapors in the headspace and place an additional load on the plant’s air-emission control system. And, air can infiltrate the headspace if the tank discharges too quickly and the liquid level drops too fast. Despite these shortcomings, however, it’s very common since can be implemented quickly and easily. Anyway, for this project, in order to give a solution to replace the current existing system, costs must be minimized, thus it will not be considered a possibility; pressure or concentration controls will certainly reduce costs.

5.6.1 Concentration control

Concentration control is suitable for unsealed tanks, which cannot hold pressure. It is very efficient: inert gas usage is optimized because it is only added when it is needed.
An oxygen analizer (Figure 5.6.1.1 a)) directly measures the actual oxygen concentration in the headspace vapor and uses it to control the flow of inert gas to the tank. The conditions of most processes are much too

harsh to permit the use of an in situ oxygen sensor. Thus, the sample-conditioning equipment (Figure Fig. 5.6.1.1 b)) is an integral part of the analyzer system. A properly designed sample-conditioning system allows the analyzer to measure reliably over a wide range of process conditions, including extremes in pressure, vacuum, and temperature, as well as in heavy-particulate and high-moisture environments.

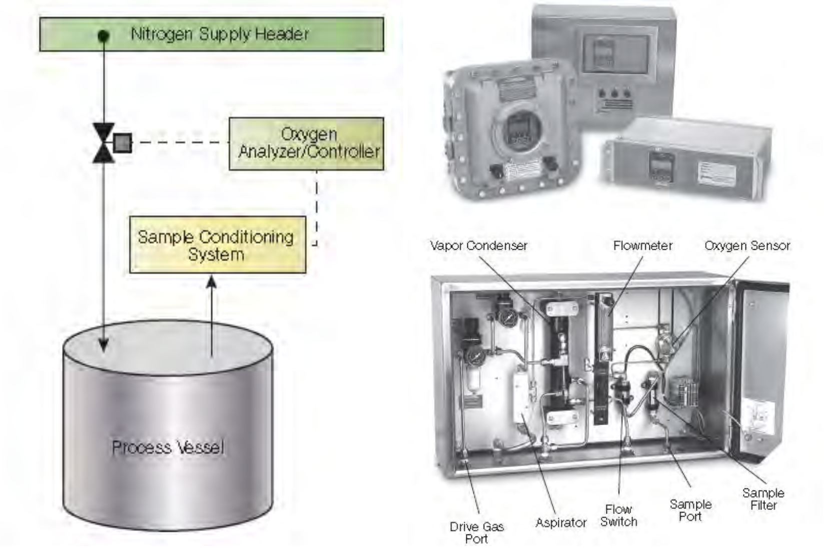


Fig. 5.6.1.1: *Concentration control a) lay-out; b) equipment.*

The advantage of continuous concentration monitoring and control is that it conserves inert gas by optimizing its usage. The savings can provide an accelerated payback on the cost of the monitoring and control equilpment. Several commercially available systems are on the market, with varying degrees of complexity and in various price ranges. The determination of the LOC for the system shall be based on the worst credible case gas mixture yielding the smallest LOC. A safety margin shall be maintained between the LOC and the normal working concentration in the system. It shall take into account the fluctuations occurring in the system, the sensitivity and reliability of monitoring and control equipment, the probability and consequences of an explosion. One of the following requirements shall be met where the oxygen concentration is continuosly monitored and controlled with safety interlocks:

1. Where the LOC is greater than or equal to 5 percent a safety margin of at least 2 volume percent below the worst credible case LOC shall be maintained;
2. Where the LOC is less than 5 percent, the equipment shall be operated at no more than 60 percent of the LOC.

In the following Tab. 5.6.1.1 are shown advantages and disadvantages of concentration control method.

Tab. 5.6.1.1: *Advantages and disadvantages of concentration control method.*

Advantages	Disadvantages
Direct measurement of the safety parameters of the process	Inadequate level of reliability of sensors that require additional security measures (continuous control of both pressure the flow of inert gas)
Minimization of the consumption of inert gas	Contamination of the sensors with the process fluid
Rapid detection of leaks and anomalies	

Because of the danger to which the production area is subjecte, is not eligible the possibility that the sensors measuring oxygen go out of order and therefore do not provide the proper monitoring atmosphere in the reactor. It is therefore recommended as a best method suited to the present situation, the inferential methods exposed in *Paragraph 5.6.2.* The inertization can be considered effective if the oxygen content is measured and maintained below the LOC, taking account of the fluctuations of the concentration of oxygen or other abnormalities that may occur during the exercise. To that end should be checked the following parameters (Figure 6):

- LOC: Limiting Oxygen concentratio (already defined);
- MAOC - (Maximum Allowable Oxygen Concentration): the maximum concentration of oxygen allowed in the machine / container that must not be exceeded, even in the presence of expected errors of operation.
- TP - Trip Point: oxygen concentration at which, the control system stops the process and puts the machine in safety / container;
- SP - Set Point: oxygen concentration at which the system controls the flow, pressure or qunato inert gas.

The relationship between these process parameters is illustrated in Fig. 5.6.1.1.

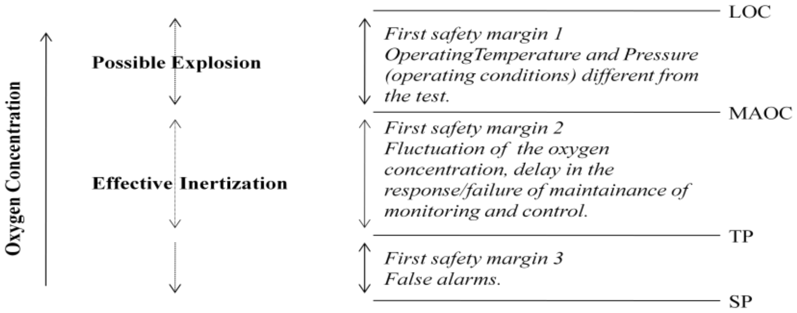


Fig. 5.6.1.1: *Operating parameters of an inerting system.*

The operational parameters should be recorded; e.g. length of time of purge, or number of pressure (or vacuum)/relief cycles. In the design calculations, it is necessary to introduce an appropriate safety margin on the LOC, already mentioned previously.

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5.6.2 Inferential methods

Among the inferential methods the prevailing, in the operations of purging, is to control the parameters of pressure within the containment of process (Fig.5.7.2.1 a)). Based on the number of cycles of purging, it is possible to determine the oxygen concentration in the final containment. These operations can be realized manually with the operator on board the reactor or, in the case of complex systems, supported by automatic systems that will have to possess certified reliability. In any case it is needed periodic monitoring with portable instrumentation, which verifies that the concentration of oxygen inside the container complies with the calculated. Pressure-control systems are employed for sealed tanks, which hold pressure: valve senses the pressure in the headspace of the tank and delivers inert gas accordingly. The headspace pressure can be set in order to guarantee a slight overpressure- but within 0,5 bar in order to not fall within the scope of the “Pressure Equipment Directive” (PED), product directive (no. 97/23 / EC) issued by the European Community, and implemented in Italy by Legislative Decree no. 93/2000. As the tank discharges, the liquid level falls, the pressure drops, and nitrogen or CO_2 is added; as the tank is filling, the pressure rises, and the gas exits through a vent valve. Several pressure-control systems are available in the marketplace, an example is shown on Fig.5.7.2.1 b).

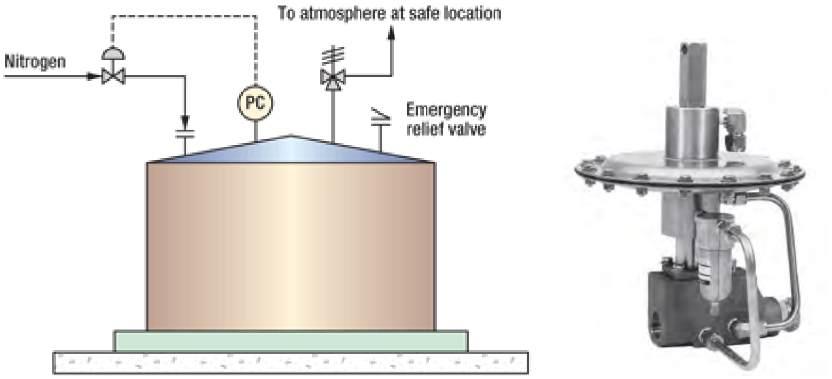


Fig. 5.7.2.1*: a) Typical pressure control system; b) Pressure control valve.*

5.7 Existing guideline

The following guidelines summarizes some prevention and protection measures for inerting systems (D.Lgs. n. 81/2008) and the classification of inerting systems according to the task (D.P.R. n. 126/1998).

5.7.1 Inertization and the D.Lgs. n. 81/2008

These provisions result from the application of Decree. N. 81/2008 and have a general validity. Specific measures are set out in the harmonized technical rules to which it belongs the UNI EN 1127-1 which is mentioned in 'Annex XLIX, Legislative Decree. N. 81/2008. The general provisions applicable, placed in the hands of the employer, are as follows:

- Choice, installation, testing, operation, inspection, testing and maintenance of work equipment, Personal Protective Equipment and electrical equipment in accordance with Title III of Legislative Decree. n. 81/2008;
- Prevention of the formation of ATEX (art. 209, paragraph I, Legislative Decree. n. 81/2008);
- Areas at risk of release of inerting gas must be fitted with alarms optical/acoustic token start and stop the system, both during the normal cycle, both during an emergency act (art. 293, D. lgs. n. 81/2008);
- Coordination between D.d.l. integrative compared to Art. 26, Legislative Decree. N. 81/2008 (art. 292 and Appendix L, Part A, Legislative Decree. N. 81/2008);
- Information and training of workers (art. 294-bis and Annex L, Part A, Legislative Decree. n. 81/2008);
- The emergency plan and evacuation must be integrated with the risk from explosion;

5.7.2 Inertization and the D.P.R. n. 126/1998

As regards the application of Directive 94/9 / EC to inerting systems must consider the three cases described below.

5.7.2.1 Preventing an explosive atmosphere

The inerting systems are designed to reduce or totally prevent the existence of an explosive atmosphere in specific areas. However, the inerting systems are not intended to stop or block incipient explosions, so they are not systems of protection under Directive 94/9 / EC. The purpose of inerting systems is different from that of the systems of explosion suppression, which can sometimes have similar parts, but which are intended to limit incipient explosion. In broad terms: inerting systems used during operation of plants etc. Not normally fall within the scope of Directive 94/9/EC.

5.7.2.2 Systems as inerting equipment

A system of inerting may (in part) also consist of parts intended to be used in a potentially explosive atmosphere and equipped potential source of ignition. These parts are to be - individually or possibly combined - in the scope of the Directive 94/9 / EC as "equipment". Again, their function of preventing a potentially explosive atmosphere by inerting is not to be assessed in the context of this Directive.

5.7.2.3 Systems of inerting as part of the system of protection against the trigger

This device, together with its inerting system, comes within the scope of Directive 94/9 / EC as part of the appliance. This inerting system is not a system of protection under Article 1.1. The component parts may be safety, control and regulation within the meaning of Article 1.2 of Directive 94/9 / EC when they are placed on the market separately. In broad terms: Directive 94/9 / EC applies to an inerting system, if this system is - or is intended to be - built-in protection system from the start of the unit and thus serves to avoid ignition sources of 'device. In some cases, these systems can be part of the system of protection against the onset of a hearing "protected by the explosions," to meet the requirements of Annex II of Directive 94/9 / EC, ie if they work as a means to protect potential sources of ignition from contact.

5.8 Industrial application – Huber process reactors

5.8.1 Inerting system choice

The type of system choosen depends on the situation of application, the following considerations were made. First of all, conditions required to use pressure purging are satisfied: the maximum and minimum pressure to which the tanks resist are, respectively, 1.5 bar and 0.1 bar. It was also calculated, as a further reason to choice, the time needed for the flushing of process reactors as following:

$t = f \cdot \frac{V}{Q} \cdot ln\left(\frac{C_0}{C_f}\right) = 2 \cdot \frac{11,7}{1,9} \cdot ln\left(\frac{21}{6,3}\right) = 15 \text{ h}$

Starting from this calculation and considering the cospicuos amount of inert gas required for the flushing process, it has been choosen the vacuum-swing purging, representing an advantage in terms of time and cost.

5.8.1 Calculation of pressure and vacuum purging cycles

In the following are calculated the numbers of cycles of theoretical purging be realized with different operating modes (pressure and vacuum) with different parameters and assumptions. The calculation is made according to the following assumptions:

- The device or from inert initially contain only atmospheric air (inerting is made before each upload);
- Transformations of gas (both in pressure is vacuum) are considered isotherms;
- Since there are no obstacles to movement or inside the units, considering the gases are mixed perfectly with each cycle, whether under pressure or depression;
- Pressures indicated (maximum and minimum) are compatible with the resistance of containments, sealing and rupture discs;
- The inerting or is made with technically pure nitrogen. It should not therefore be present initial contamination of oxygen.

Preliminarily is determined the LOC of the mixture N_2 / air and CO_2 / air using an adequate margin of safety in the experimental value C_C (Tab. 5.2.1) according to Standard NFPA 69. It is:

$$C_N = C_C - 2$$

Tab. 5.11.1.1: *Limiting Oxygen Concentration in Nitrogen and Carbon Dioxide.*

Inert gas	**N_2**	**CO_2**
C_N	7 %	11 %

Given these assumptions, purging cycles calculated are shown in Table 5.11.1.1.

Tab. 5.11.1.1: *Simulation of the concentrations of oxygen to vary the number of cycles of inerting.*

Minimum and Maximum Pressure (Absolute)	**Oxygen concentration (% VOL.) variation according to number of cycles**							
	0	1	2	3	4	5	6	7
P_{max}=3,0 bar P_{min}=1,0 bar	21,00	7,0	2,33	0,78	0,26	0,09	0,03	0,01
P_{max}=2,5 bar P_{min}=1,0 bar	21,00	8,40	3,36	1,34	0,54	0,22	0,09	0,03
P_{max}=2,0 bar P_{min}=1,0 bar	21,00	10,50	5,25	2,63	1,31	0,66	0,33	0,16
P_{max}=1,5 bar P_{min}=1,0 bar	21,00	14,00	9,33	**6,22**	4,15	2,77	1,84	1,23
P_{max}=1,0 bar P_{min}=0,7 bar	21,00	14,70	10,29	7,20	5,04	3,53	2,47	1,73
P_{max}=1,0 bar P_{min}=0,6 bar	21,00	12,60	7,56	4,54	2,72	1,63	0,98	0,59
P_{max}=1,0 bar P_{min}=0,5 bar	21,00	10,50	5,25	2,63	1,31	0,66	0,33	0,16
P_{max}=1,0 bar P_{min}=0,4 bar	21,00	8,40	3,36	1,34	0,54	0,22	0,09	0,03
P_{max}=1,0 bar P_{min}=0,3 bar	21,00	**6,30**	1,89	0,57	0,17	0,05	0,02	0,00
P_{max}=1,5 bar P_{min}=0,3 bar	21,00	4,6	1,32	0,66	0,53	0,5	0,5	0,5
P_{max}=1,0 bar P_{min}=0,2 bar	21,00	4,20	0,84	0,17	0,03	0,01	0,00	0,00
P_{max}=1,0 bar P_{min}=0,1 bar	21,00	2,10	0,21	0,02	0,00	0,00	0,00	0,00

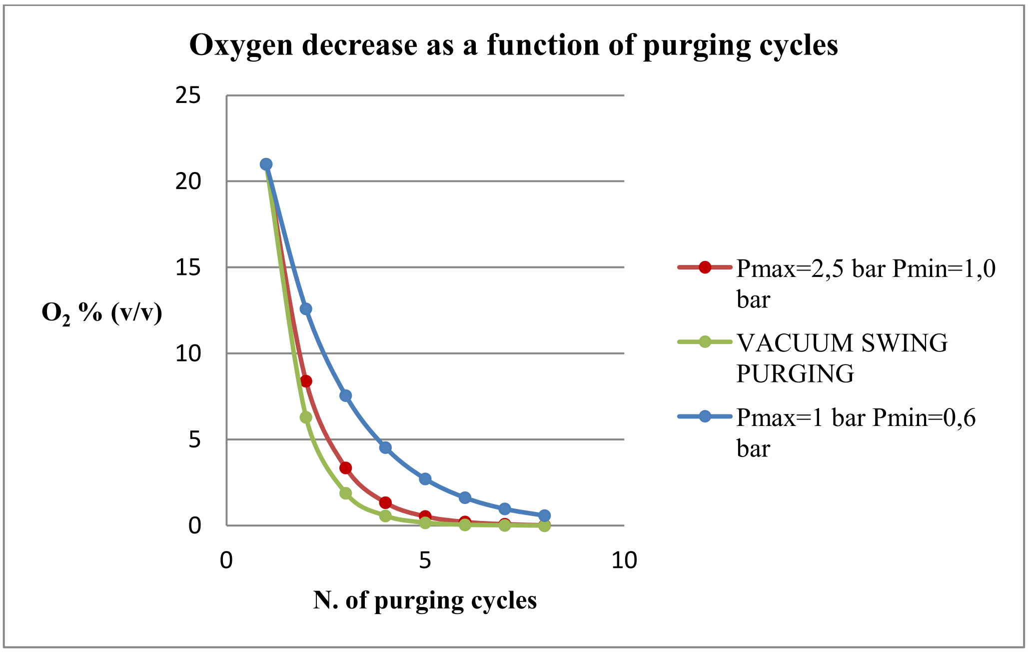
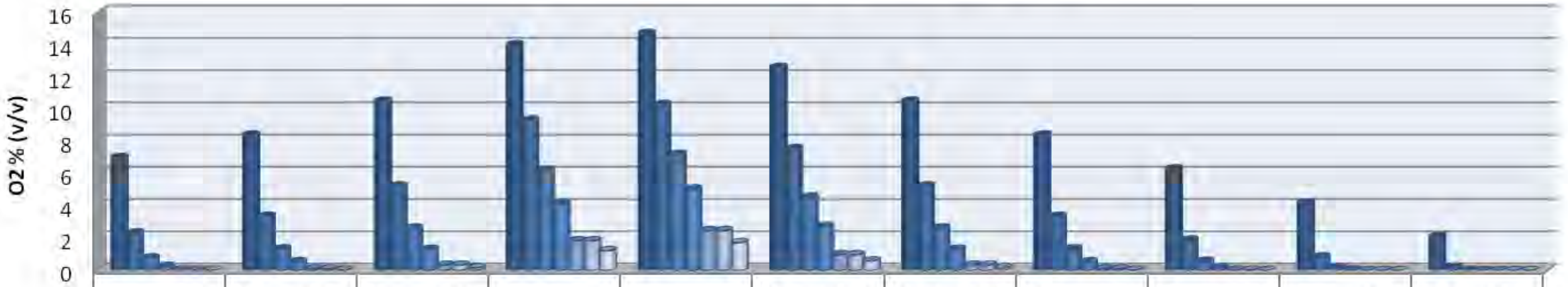


Fig 5.11.1.1: *Oxygen decrease according to purging cycles.*

In Tab. 5.11.2.7.1 are shown the volumes value of tanks located in the workplace area. As it can be seen from the table, sixtyfour process reactors need to be inerted.

Tab. 5.11.2.7.1: *Tank's volume in production area.*

Plant 1										**Plant 2**	
Bay 1		**Bay 2**		**Bay 3**		**Bay 4**		**Bay 5**		**Bay 1**	
Process tank	**Volume (m^3)**	**Process tank**	**Volume (m^3)**	**Process tank**	**Volume (m^3)**	**Process tank**	**Volume (m^3)**	**Process tank**	**Volume (m^3)**	**Process tank**	**Volume (m^3)**
I5	6,9	I7	6,9	F35	8,2	ST6	10	I20	50	D10	23
F5	6,9	F7	6,9	I27	7,1	ST5	10	F20	50	D6	11,7
F4	6,9	D3	5	I26	7,1	ST4	10	ST8	60	D/	11,7
I4	6,9	D2	5	F33	8,2	D5	10,5	ST7	60	F29	6,5
I3	6,9	I10	10	F38	8,2	F19	8	F21	15	F30	6,5
F3	6,9	F10	11,1	I28	7,1	I19	6			F31	6,5
F2	6,9	I9	11,1	F36	8,2	I18	10,5			F32	6,5
I2	6,9	F9	11,1	F34	8,2	F18	10			F24/A	12,8
I1	6,9	F8/A	9,8	F37	8,2					F24/B	12,8
F1	6,9	I8	9							I23	11,7
F6	8,2	F8/B	9,8							I22	11,7
I6	11,1	I11	9,9							F23/A	12,8
D1	11,1	F11	10,5							F23/B	12,8
										F22/A	12,8
										F22/B	12,8
										I21	11,7


O2% variations according to purging cycles

	Pmax=3,0 bar Pmin=1,0 bar	Pmax=2,5 bar Pmin=1,0 bar	Pmax=2,0 bar Pmin=1,0 bar	Pmin=1,5 bar Pmin=1,0 bar	Pmax=1,0 bar Pmin=0,7 bar	Pmax=1,0 bar Pmin=0,6 bar	Pmax=1,0 bar Pmin=0,5 bar	Pmax=1,0 bar Pmin=0,4 bar	Pmax=1,0 bar Pmin=0,3	Pmax=1,0 bar Pmin=0,2 bar	Pmax=1 bar Pmin=0,1 bar
■ N=1	7	8,4	10,5	14	14,7	12,6	10,5	8,4	6,3	4,2	2,1
■ N=2	2,33	3,36	5,25	9,33	10,29	7,56	5,25	3,36	1,89	0,84	0,21
■ N=3	0,78	1,34	2,63	6,22	7,2	4,54	2,63	1,34	0,57	0,17	0,02
■ N=4	0,26	0,54	1,31	4,15	5,04	2,72	1,31	0,54	0,17	0,03	0
■ N=5	0,03	0,09	0,33	1,84	2,47	0,98	0,33	0,09	0,02	0	0
□ N=6	0,03	0,09	0,33	1,84	2,47	0,98	0,33	0,09	0,02	0	0
□ N=7	0,01	0,03	0,16	1,23	1,73	0,59	0,16	0,03	0	0	0

In the light of the results it can be made the following considerations:

- At constant pressure jump, the vacuum operations require a smaller number of cycles to reach the concentration of oxygen demand. For example, by comparing the cycle under vacuum at 0.3 bar with that in pressure to 1.5 bar only one cycle is needed to reach the concentration of oxygen of 6,3 % through vacuum purging, on the other hand it requires n. 3 cycles in the case of pressure purging;
- The average concentration at the end of each cycle is only dependent on the ratio of the pressure and is independent from the volumes to be inertized. The parameter that varies will instead be the duration of the cycle, depending on this parameter the ratio between the inerting volume and the flow of inert gas.

5.11.2 Inert gas requirement

The amount of gas required to blank a tank under pressure control is the sum of the gas required based on tha tank's working throughput (N_W) and the one required by thermal breathing, i.e., the rise and fall of the liquid level due to the external temperature changes (N_{TB}). So the total gas requirement:

$$N_T = N_W + N_{TB} \quad \text{Eq. 5.9}$$

Defining:

$$N_W = \frac{V_T}{7{,}48} \quad \text{Eq. 5.10}$$

$$N_{TB} = V_{HS} * \left(\frac{Tmax - Tmin}{555}\right) * \left(\frac{1}{7{,}48}\right) * F \quad \text{Eq. 5.11}$$

N_T Total volume of gas required per production;
N_w Inert Gas required by the material flow through the tank;
N_{TB} Inert Gas required by thermal breathing;
V_T Total volume of material discharged from the tank per production;
V_{HS} Average empty space;
T_{max} Maximum temperature in the tank;
T_{min} Minimum temperature in the tank;
F Estimated number of temperature swings per production.

Peak nitrogen usage is associated to rapid temperature changes:

$$Nmax = 8{,}021 * P + 0{,}02382 * C \quad \text{Eq. 5.12}$$

Where:

N_{max} Maximum nitrogen flowrate
P Pump-out rate
C Total tank capacity

In terms of numbers, in the Tab. 5.11.2.1 are reported estimations of inert gas:

Tab. 5.11.2.1: *Inert gas quantities estimation.*

PARAMETER	VALUE	U.M.
V_T	**9,4**	**m^3**
N_{TB}	0,3	m^3
T_{max}	70	°C

T_{min}	6	°C
F	1	
V_{HS}	2,3	m^3

Requirements of gas has been calculated (Tab. 5.11.2.2 and Tab. 5.11.2.3) for both mixing and refining reactors of all the production area. Referring to the calculations performed, it is stressed that it has been considered the volume due to the emptying of the mixing vessel and the volume due to the emptying of the finishing tank multiplied by the number of steps required for the concentrated pulp manufacturing. Infact, during the finishing phase, the ink undergoes turnovers from one reactor to another one for the purpose of achieving the desired product characteristics. These turnovers range from color to color and from series to series. The tables reported in Annex II show the quantities of total inert gas required for each production, number of turnovers of the finishing phase, total production per year; taking also into account the annual production of inks for the year 2014, it is estimated an average annual need:

Tab. 5.11.2.7.1: *Yearly inert gas requirement estimation.*

Machine	Number of turnover/output	Losses/production	Total production in year 2014	Total Inert gas requirement
Bay 1				
Drais 1	2	22,6 Nm^3	26	**1.581 Nm^3**
Drais 2	2	17 Nm^3	15	**1.860 Nm^3**
Drais 3	15	93 Nm^3	17	**1.581 Nm^3**
Drais 4	13	93 Nm^3	20	**2.551 Nm^3**
Drais 5	15	93 Nm^3	17	**588 Nm^3**
M13	2	18 Nm^3	72	**1.296 Nm^3**
D1	1	9,3 Nm^3	113	**1.051 Nm^3**
Bay 2				
N10	13	81 Nm^3	15	**1.215 Nm^3**
D3	/	4 Nm^3	173	**Nm^3**
D2	/	4 Nm^3	191	**764 Nm^3**
N9	7	52 Nm^3	26	**1.352 Nm^3**
N8	5	25 Nm^3	35	**875 Nm^3**
N12	4	41 Nm^3	92	**3.772 Nm^3**
N6	9	59 Nm^3	27	**1.585 Nm^3**
Bay 3				
N18	5	33 Nm^3	167	**5.477 Nm^3**
N19	9	52 Nm^3	102	**5.232 Nm^3**
N20	5	33 Nm^3	129	**4.257 Nm^3**
Bay 4				
D5	/	6,5 Nm^3	191	**1.242 Nm^3**
M11	2	27 Nm^3	15	**5.477 Nm^3**
N14	5	24 Nm^3	44	**5.232 Nm^3**
ST6	/	8,4 Nm^3	Variable	**8,4 Nm^3**
ST5	/	8,4 Nm^3	Variable	**8,4 Nm^3**
ST4	/	8,4 Nm^3	Variable	**8,4 Nm^3**
Bay 5				
M12	2	153,7 Nm^3	72	**2.808 Nm^3**
Plant 2-Bay1				
D10	/	21 Nm^3	287	**6.027 Nm^3**
D6	/	9,7 Nm^3	222	**2.153 Nm^3**
D7	/	9,7 Nm^3	222	**2.153 Nm^3**
F29	/	5,3 Nm^3	108	**572 Nm^3**
F30	/	5,3 Nm^3	68	**360 Nm^3**

F31	/	5,3 Nm^3	80	**424 Nm^3**
F32	/	5,3 Nm^3	36	**191 Nm^3**
N16	5	65 Nm^3	77	**7.884 Nm^3**
N13	5	65 Nm^3	62	**4.030 Nm^3**
N15	13	146 Nm^3	54	**5.005 Nm^3**
Yearly estimation gas requirement				**69.609 Nm^3**

5.11.3 Powder substances loading

5.11.3.1 Inert gas flowrate

The addition of solids through the loading hopper (Fig. 5.12.1) within an inertized vessel involves opening towards the atmosphere and inevitably the entry of air, therefore a raising of the level of oxygen that might exceed the value of LOC and generate, then, an explosive atmosphere.

Fig. 5.12.1*: Loading hopper.*

With reference to section 5.11.1, they were quantified purging to reach the desirable LOC security. Assuming an a vacuum purging, it is seen that to reach the LOC of 6,3 % is required a cycle of pressurization (Pmax = 1.0 bar and Pmin = 0.3 bar). The data in characterizing the loading of pigments are the following:

Tab. 5.11.3.1: *Pigment and nitrocellulose input data.*

	Nitrocellulose	**Pigment Blu**
Density	1.650 Kg/m^3	860 Kg/m^3
Mass of solid	4.161 Kg	3.200 Kg
Big-bag weight	25 Kg	250 Kg
Big-bag loading time	0,08 h	0,08 h
Solid flowrate	312,5 Kg/h	3.125 Kg/h
Oxygen content in air	21 %	

Two systems for loading management has been evaluated.

a. Double valve device

To avoid the entrance of air into the tank, it can be used a device with double valve: with bottom valve closed, the valve top is open and are paid out in space inter-valves solids; subsequently it is closed again the upper valve and opened the lower one by dropping the solids into the vessel. In this way it is introduced into the inerted atmosphere of the vessel only the air contained in the bodies of the incoherent solid.

$$V_n = V^* \cdot \left(\frac{1 - exp\left(\frac{-Q \cdot n \cdot t^*}{U}\right)}{1 - exp\left(\frac{-Q \cdot n \cdot t^*}{U}\right)} \right) + V_0 = 0{,}017m^3 \cdot \left(\frac{1 - exp\left(\frac{-2\frac{m^3}{h} \cdot 12{,}8 \cdot 1{,}05h}{6m^3} \right)}{1 - exp\left(\frac{-2\frac{m^3}{h} \cdot 12{,}8 \cdot 1{,}05h}{6m^3} \right)} \right) + 025m^3$$

$$= 0{,}3\ m^3$$

Vn volume of oxygen after n loadings of solids;

$V^* = 0{,}03\ m^3$

Volume of oxygen during each loading of solids (250 Kg bags).The value is determined by considering the density of powder = 1.553 kg / m^3, assuming the fraction of air in the mass of powder = 0.5 and the fraction of oxygen in air = 0.21, which yields:

$$V^* = \frac{250}{1.553} * 0{,}5 * 0{,}21 = 0{,}03m^{3^*};$$

$Q = 3{,}5\frac{m^3}{h}$ Inert gas flowrate;
$n = 12{,}8$ Number of solids loading;
$t^* = 1{,}06\ h$ Solids loading time (t^* = (12,8*5 min)/(60min) = 1,06 h);
$U = 6\ m^3$ Free volume;
$V_0 = 0{,}24\ m^3$ Initial volume of oxygen in the tank (V_0= 3,8 m^3 · 6,3%).

At the end of the n positions the oxygen concentration in the machine applies:

$$C = \frac{V_n}{U} \cdot 100 = \frac{0{,}3\ m^3}{3{,}9\ m^3} = 6{,}7\ \%$$

b. Inertization of the loading hopper

The Volumetric Flow (VF) input required to maintain the mixture below the LOC is the following:

$$VF = \frac{Solid\ flowrate}{Density} = 3{,}5\frac{m^3}{h}$$

Assuming that 50% of this volume is composed of air, it is obtained that the oxygen (G) input is equal to:

$$G = \frac{3{,}5}{2} * 0{,}21 = 0{,}4\ \frac{m^3}{h}$$

If the input amount of oxygen must be proportional to the value considered safe for the mixture (7 %), it is obtained that the flow (FT) must be equal to:

$$FT = \frac{100 \cdot 0{,}2}{7} = 5{,}2\ \frac{m^3}{h}$$

The total nitrogen flow input will be equal to:

$$NF = 0{,}95 \cdot 5{,}2 = 5\ \frac{m^3}{h}$$

Given that the incoming air has about 79% of nitrogen, the flow rate of nitrogen additional to keep the mixture inerted will be equal to:

$$QNA = 2{,}7 - \frac{3{,}15}{2} \cdot 0{,}79 = 3{,}5\ \frac{m^3}{h}$$

The load of dust from the manhole is inherently dangerous to both the possibility of losing the inert atmosphere to the risk of suffocation staff (anoxia). To mitigate the first risk it is necessary to ensure a slight overpressure, in order to obstruct the entry of oxygen during the opening of the manhole; with regard to the second risk, it will install a system of local exhaust, suitably sized, near the manhole.

5.11.4 Injection verification

Once an inert atmosphere has been established, its presence needs to be verified before any flammable materials are admitted. There is the possibility of stratification with flow through inerting, and air ingress with all methods of creating the inert atmosphere. Assuming a stationary condition at temperature of 10 °, that is the one referred temprature when download is completed, the mixture vapor - inert gas mixture is the following:

$$P_{tot} = P_{vapors} + P_{inert\ gas} = 0{,}03 \text{ bar} + 1{,}1 \text{ bar} \sim 1{,}1 \text{ bar}$$

This verification is valid for any temperature, the latter being represented only a multiplicative factor in the relationship of an ideal gas. In both cases the result is that the density of the inert gas is greater than the vapor therefore it is advisable insufflation from the top down to avoid stratification inside the head of the tank thereby suppressing the creation of hazardous atmospheres. Anyway, this represents only a theoretical result, in order to verify on reality, it's advisible to perform gas sampling within the vessel even to confirm the adequacy of the vessel inerting process. Test for density stratification within the vessel by taking measurements at different elevations. If at all possible, measurements should be taken all the way down to the floor of the vessel.

- Test for stagnant zones within the vessel by taking measurements at different horizontal locations.
- Test for changes in gas composition over time. do not assume that the gas composition is constant over time.

Anyway, continuos mixing process would help to avoid stratification and guardìantee an homogenous inert atmosphere.

5.11.5 Measures to be taken in case the inerting system fails. Existing guideline

The modification of the current Exhaust System, in terms of fire risk, does not change the Fire Prevention Certificate. As soon as this system has been adepted and installed, a new risk assessment document must be drafted, entering the change to the current system. Several guidance documents exist to aid the designer in inerting vessels:

- Factory Mutual. Property Loss Prevention Data Sheets. 7-59. 1977, recised 1998. Inerting and Purging of Tanks, Process Vessels and Equipment.
- 2. VDI 2263 Part 2, 1992. Dust Fires and Dust Explosions: Hazards – Assessment – Protective Measures.
- 3. Guide to Dust Explosion Prevention and Protection. Part 2 – Ignition Prevention, Containment, Inerting, Suppression and Isolation. C. Schofield and J. A. Abbott. Institution of Chemical Engineers.
- NFPA 69, 1997. Standard on Explosion Prevention Systems
- ESCIS Booklet 3, 1994. Inerting. Methods and Measures for the Avoidance of

No single document, however contains all the necessary information. The goal of all these documents is the same: provide guidance on how to displace or dilute the vessel's, equipment's, or pipe's internal oxygen and/or flammable vapor concentration.

5.11.6 Losses estimation

In order to estimate emission losses during a production activity, has been applied a software, which is suitable for the situation in exam. TANKS PROGRAM is a computer-based software developed by the American Petroleum Institute (API) to use site-specific information to predict emissions from petroleum production storage tanks according to API650 and API 653 codes. It estimates flashing, working and standing losses and calculates losses using specific operations for each user's tank. It has been developed for petroleum products, but it is adopted for the design of tanks containing organic liquid storage too.
Total emissions are quantified as two contributions:

$$L_{tot} = L_w + L_s \qquad \text{Eq. 5.16}$$

Fig. 5.11.6.1: *Reactors emissions.*

5.11.6.1 Volumetric expansion losses

The "ingredients" required for the processing are loaded in the tanks at a temperature similar to that external, therefore considering the winter months as those most unfavorable conditions, it is referred to a temperature of the product corresponding to about 6-10 °. The heating of the reactors and the subsequent mixing, increases the temperature of the liquid mixture to around 40-45 °. During this heating occurs a thermal expansion volume which will cause the loss of gas through the vents.
By defining the volume change according to the equation following:

$$\Delta V = \alpha \cdot V_0 \cdot \Delta T$$

Where:

ΔV Volume variation due to thermal expansion;
α Thermal expansion coefficient;
V_0 Initial volume;
ΔT Temperature variation.
Losses due to thermal expansion has been calculated:

Tab. 5.11.6.1: *Volume expansion due to temperature increase.*

Process reactor	V_0	ΔT	α	ΔV
Mixing	2,3 m^3	50 °C	$3{,}6 \cdot 10^{-3}$ °C^{-1}	0,4 m^3
Finishing	2,5 m^3	50 °C	$3{,}6 \cdot 10^{-3}$ °C^{-1}	0,45 m^3

5.11.6.2 Working losses

Losses due to the lowering of the liquid level whereas the pressure within the tank equal to 1,1 bar which is equal to that in the liquid level and assuming the tank in the case of higher temperature ie at T = 45 ° in phase dough and T = 65 ° in the finishing phase:

$$L_w = 0{,}001 \cdot M_{VA} \cdot P_{va} \cdot Q \cdot K_n \cdot K_p \qquad \text{Eq. 5.17}$$

Applying Eq. 5.17, the losses of the mixing tank are quantified as follows (Tab. 5.11.6.2.1 and Fig. 5.11.6.2.1):

Table 5.11.6.2.1: *Working losses of mixing reactor.*

	Meaning	Value	U.M.
M_{VA}	Vapor molecular weight	29,8	g/g*mol
P_{VA}	Vapor pressure at daily average liquid T	1,1	bar
Q	Production net throughput	9,42	m^3
K_N	Working loss turnover	1	
N	Number of turnovers	1	
V_{LX}	Tank maximum liquid volume	9,4	m^3
K_P	Working loss product factor	1	
T_{LA}	Daily average liquid surface	45	°C
W_V	Vapor density	0,1	Kg/m^3
L_W	Working losses	**4,5**	m^3/output

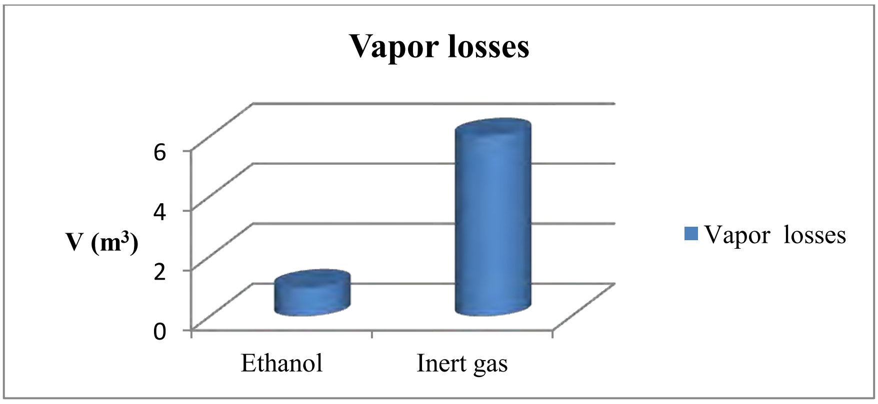


Fig. 5.11.6.2.1: *Components vapor losses.*

Losses of the finishing tank are quantified as follows (Tab. 5.11.6.2.2 and Fig. 5.11.6.2.2):

Table 5.11.6.2.2: *Working losses of finishing reactor.*

	Meaning	Value	U.M.
M_{VA}	Vapor molecular weight	29,8	g/g*mol
P_{VA}	Vapor pressure at daily average liquid T	1,1	bar
Q	production net throughput	10,4	m^3
K_N	Working loss turnover	1	

N	Number of turnovers	1	
V_{LX}	Tank maximum liquid volume	10,4	m^3
K_P	Working loss product factor	1	
T_{LA}	Daily average liquid surface	57	°C
W_V	Vapor density	0,1	Kg/m^3
L_W	Working losses	**5**	m^3/output

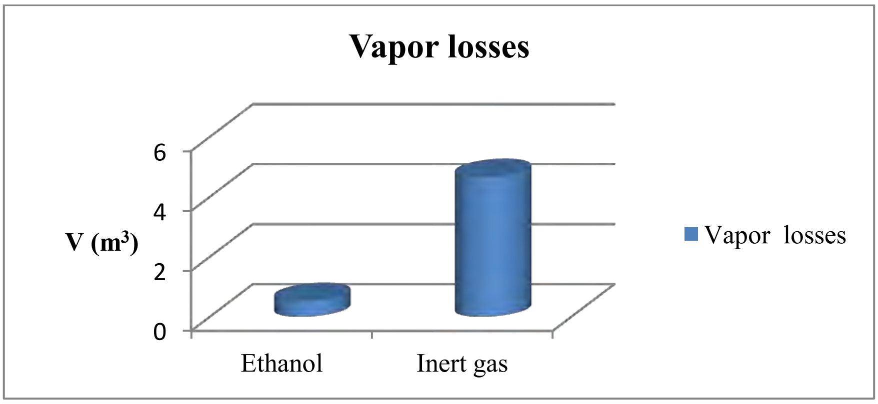


Fig. 5.11.6.2.2: *Components vapor losses.*

The losses of the tanks are also overestimated of about 2-3 m^3/production during emptying due to an hypotetical delay of the worker (5-10 s) to close the valve. The Tab. 5.11.6.3 provides an estimate of losses of tanks (64) in the production area.

Tab. 5.11.6.3: *Process reactor's yearly working losses estimation.*

Machine	Number of turnover/output	Losses/production	Total production in year 2014	Total Inert gas requirement
Bay 1				
Drais 1	2	7,3 Nm^3	26	**190 Nm^3**
Drais 2	2	7,3 Nm^3	15	**110 Nm^3**
Drais 3	15	40 Nm^3	17	**680 Nm^3**
Drais 4	13	35 Nm^3	20	**700 Nm^3**
Drais 5	15	40 Nm^3	17	**677 Nm^3**
M13	2	7 Nm^3	72	**504 Nm^3**
D1	1	4,2 Nm^3	113	**475 Nm^3**
Bay 2				
N10	13	38	15	**570 Nm^3**
D3	/	2	173	**346 Nm^3**
D2	/	2	191	**382 Nm^3**
N9	7	20	26	**520 Nm^3**
N8	5	16	35	**560 Nm^3**
N12	4	19	92	**1.748 Nm^3**
N6	9	23	27	**621 Nm^3**
Bay 3				
N18	5	14	167	**2.338 Nm^3**
N19	9	17	102	**1.734 Nm^3**
N20	5	14	129	**1.806 Nm^3**
Bay 4				
D5	/	2	191	**382 Nm^3**
N10	2	8	15	**120 Nm^3**
N14	5	23	44	**1.012 Nm^3**

Bay 5				
M12	2	**39**	**72**	**2.808 Nm^3**
Plant 2-Bay1				
D10	/	9,8	287	**2.813 Nm^3**
D6	/	4,4	222	**977 Nm^3**
D7	/	4,4	222	**977 Nm^3**
F29	/	2,4	108	**260 Nm^3**
F30	/	2,4	68	**163 Nm^3**
F31	/	2,4	80	**144 Nm^3**
F32	/	2,4	36	**86 Nm^3**
N16	5	31	77	**2.387 Nm^3**
N13	5	29	62	**1.798 Nm^3**
N15	13	67	54	**3.618 Nm^3**
Overall Losses				**31.555 Nm^3**

Tab. 5.11.6.3: *Yearly tank's losses estimation.*

Losses due to an hypothetical delay of the worker (~2 Nm^3/ production)	**37.105 Nm^3**
Tank's losses	31.555 Nm^3
Losses due to vapor expansion	2.028 Nm^3
Total losses	**70.688 Nm^3**

One consideration is the amount of losses if related to CO$_2$ or N$_2$. Carbon dioxide has a molecular weight than nitrogen maggiroe therefore you will have more losses during the emptying of the tanks, the other side instead of N losses predominate during tankage therefore to consider taking the same loss, but please consideration that the carbon dioxide is semza doubt preferable, both for volatility that for dangerousness.

5.11.6.2 Standing losses

Standing losses are a result of tank vapor space breathing. They are the most hardly characterizable because depend on the setting pressure range etc .. The program quantifies the losses for storage TANKS therefore subject to the containment of the mixture for too long time and continuous that has no veracity in being compared to the case in question; in fact the mixing process has a duration of about two hours therefore, in first approximation, they can be neglected. The same reason applies for the finishing tank, but in this case, being the duration of the latter phase of the order of days, it is applied a correction factor of 1.2 / 1.5 to the working losses

Chapter 6. Inertization Risk Assessment and Results comparison

Huber Italy is a chemical that daily employs flammable and explosive substances for the production of inks, so the risk in working environment can never be reduced to a level lower than the high. Recalling the Machinery Directive 459/96, "*The machinery must be designed and constructed to avoid any risk of explosion posed by the machinery itself or by gases, liquids, dust, vapors or other substances produced or used by the machinery. To this end the manufacturer must take the necessary measures to:*

- *Avoid a dangerous concentration of products,*
- *Prevent combustion of the explosive,*
- *Reduce the consequences of a possible explosion so that it does not endanger the surroundings. If the manufacturer foresees the use of the machine in an explosive atmosphere, the same precautions will be taken.* "

In addition, "*The machinery must be designed, constructed and / or equipped as to minimize the risks due to gases, liquids, dusts, vapors and other waste products. Where a hazard exists, the machinery must be equipped in such a way can be contained and / or evacuated these products.* "

This last sentence was intended to refer to the preventive system in current use, but to demonstrate the benefit that this proposed design solution brings, it is performed a risk analysis, in accordance with the Machinery Directive 459/96, of the process reactor. The risk analysis is conducted according to the following criteria:

- Determination of the operation of the machine.
- Hazard identification.
- Risk Estimate
- Risk assessment and the potential serious consequences.

Figure 6.1.1 represents the steps for the choice of integrated preventive measures. If the machine works under an inert atmosphere, the technical file must be drawn up and inserted:

- A copy of the manual of instructions for use of the machine. (Res all.1 1.7.4**).** (Document to be delivered to the user together with the declaration of conformity**)**
- Construction drawings**;**
- Calculations;
- Sizing machine;
- The risk analysis performed by the manufacturer;
- The measures to eliminate the risks;
- Any residual risks can not be eliminated and the related instructions to avoid dangers deriving from the latter.

The Instruction Manual must:

- Take into account the safety of the operators during the entire life cycle of the machine;
- Provide technicians, operators, and maintainers all the information and warnings relating to 'use in safety conditions of the machine.

General information:

- Field of use of the machine;
- Operators required (specialist);
- Arrangements by the user 's;

- Technical assistance;
- Mode of handling.

Description of the machine:

- Illustrations;
- Technical data;
- Guaranteed performance

Injury Prevention:

- Conditions for safe use;
- Personal protective equipment prescribed;
- Intended uses;
- Use not provided;
- Work zones;
- Hazardous areas;
- Plates;

Residual risks installation:

- Packaging;
- Shipping;
- Transport;

Operation:

- Set-up for the first start;
- Commands and dangerous areas;
- Description of the framework and layout of the controls;
- Operating modes;
- Normal stop and emergency;
- Management of the material used and the product;

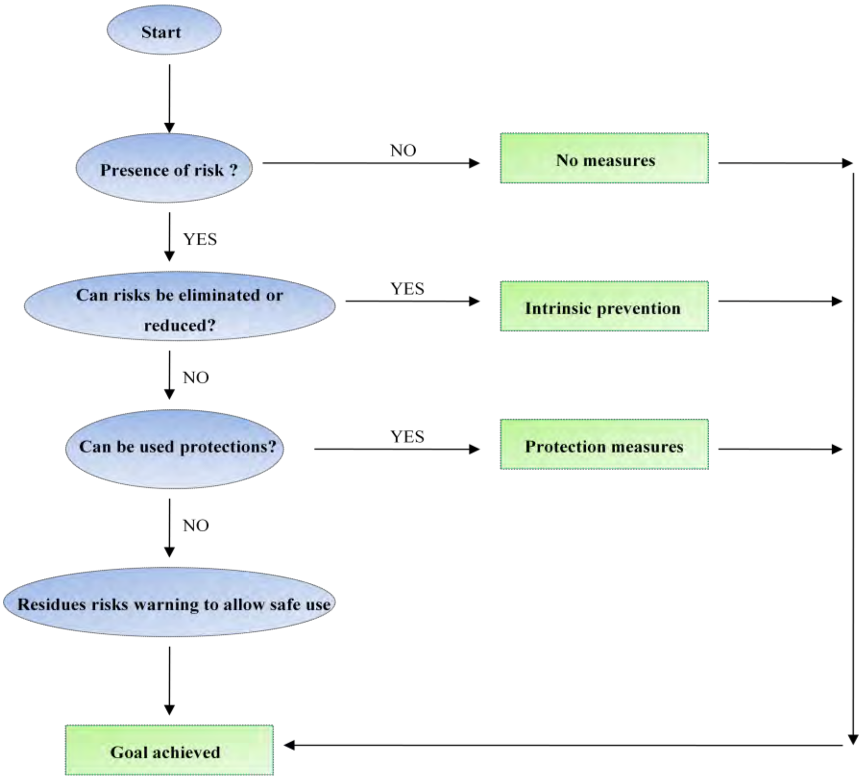


Fig. 6.1.1: *Schematic representation for the choice of preventive integrated measures.*

6.1 Risk quantification

With the purpose of demonstrating in concrete terms the actual improvement of the adoption of the inertization, it was determined the residual risk of tanks blanketed**.** Risk assessment is made in accordance with the following assumptions: GOOD availability of inertization service or assuming in case of interruption of service, the adoption of substitute protection. (f.e. automatic shutdown of the process). The same procedure used for risk quantification defined in *Chapter 4* has been adopted and results obtained. To define the residual risk of fire in quantitative terms, it is used the mathematical model of BM systems that defines it:

$$RR = C_i * F_m * F_C$$

where:
C_i Fire load expressed in Kg of wood or equivalent Standard / m2; Standard/m^2;
F_m Product of multiplying factors of risk that represent the parameters responsible for the increase in the fire risk. It is the term connected to the MAGNITUDO ;
F_c Factor of risk compensation related with all the parameters that contribute to the mitigation of risk. It is the term connected to the FREQUENCY.

6.1.2 Fire load

Inerting tanks eliminate one of the three elements of the fire triangle, the comburent (oxygen), however, the fire load is unchanged. Tab. 6.1.2.1 shows the fire load already defined in Chapter 5. The specific fire load rating q_f expressed in Kg of wood or equivalent standard/m^2 is defined as:

Tab. 6.1.2.1: *Specific fire load of design.*

Area/Sector	Function	Specific fire load of design MJ/m^2	Class
Factory n.1- Bay 1	Production area	3.001	240
Factory n.1- Bay 2	Production area	2.747	240
Factory n.1- Bay 3	Production area	1.687	120
Factory n.1- Bay 4	Production area	4.760	240
Factory n.2- Bay 1	Production area	5.451	180
Factory n.2- Bay 2	Production area & Warehouse	2.254	240
Factory n.2- Bay 3	Warehouse	7.835	240
Factory n.2- Bay 4	Warehouse	7.835	240
Factory n.2- Bay 5	Warehouse	8.075	240
Factory n.2- Bay 5	Warehouse	7.613	240

The level of residual risk, based on the result obtained from the formula given above, can be obtained by applying the following criteria (Tab. 6.1.2.2):

Tab. 6.1.2.2: *Criteria for residual risk classification.*

RR	Level of residual risk
< 20	Low
20-50	Medium
>50	High

6.1.3 Multiplying factors of risk

The multiplying factors of risk are those parameters responsible of fire risk increase. They are directly connected to the concept of MAGNITUDO. The magnitude of the consequences can be expressed for example as a function of the number of parties involved in this type of risk and the level of damage caused to them.

Tab. 6.1.3: *Mutiplying factors of risk.*

Multiplying factors of risk		
PARAMETER	**DEFINITION**	**VALUE**
Burning rate	R_c	1,5
Toxicity of the combustion products	P_f	2
Probability of initiation	Pi	1,6
Probability of personal injury	P_{aff}	1

6.1.4 Risk compensation factor

The compensation factor of the fire risk is related with the environmental conditions, the fire safety facilities and management organization of the work, in all aspects of fire prevention, these parameters, identifiable with the responses to each question, the text of which It is reported in separate grids by subject. Each single response contributes for a portion equal to 1 / n, where n is the total number of questions. The compensation factor is obtained, then, with the following algorithm:

$$F_c = 1 - \frac{\sum_{i=1}^{10}\left(D_{ok}(P_s)\right)i}{\sum_{i=1}^{10}\left(N_{tot}(P_s)\right)i} = 0{,}05$$

Tab. 6.1.4.1: *Risk compensation factor parameters.*

Compensation factor	
PARAMETER	**DEFINITION**
D_{ok}	Number of questions with an affermative answer
N_{tot}	Total number of questions to answer than "QUESTION IS NOT APPLICABLE TO THE SECTOR UNDER CONSIDERATION"

The 10 parameters P_s originating the compensation factor of the fire risk are:

- Probability of initiation;
- Features of the buildings and premises;
- Security operating procedures and working;
- Conditions and likelihood of exodus;
- Maintenance;
- Alarm;
- Antifire;
- Control;
- Security management and emergency;

In addition, considering the estimated fire load, areas are classified according to fire resistance classes.

6.1.5 Results

Residual Risk (RR) has been quantified as:

$$RR = C_i * R_C * P_f * P_i * P_{aff} * F_c$$

The risk level of each area, so, is summarized in Tab. 6.1.5.1:

Tab. 6.1.5.1: *Characterization of the Residual Risk of each area.*

Area/Sector	Function	Residual Risk
Factory n.1- Bay 1	Production area	39
Factory n.1- Bay 2	Production area	36
Factory n.1- Bay 3	Production area	22
Factory n.1- Bay 4	Production area	49
Factory n.2- Bay 1	Production area	29
Factory n.2- Bay 2	Warehouse	51
Factory n.2- Bay 3	Warehouse	102
Factory n.2- Bay 4	Warehouse	102
Factory n.2- Bay 5	Warehouse	105
Factory n.2- Bay 6	Warehouse	99

Detailed calculations are included in Annex I. The results have been plotted in the following graphs (Fig. 6.1.5.1 and 6.1.5.2):

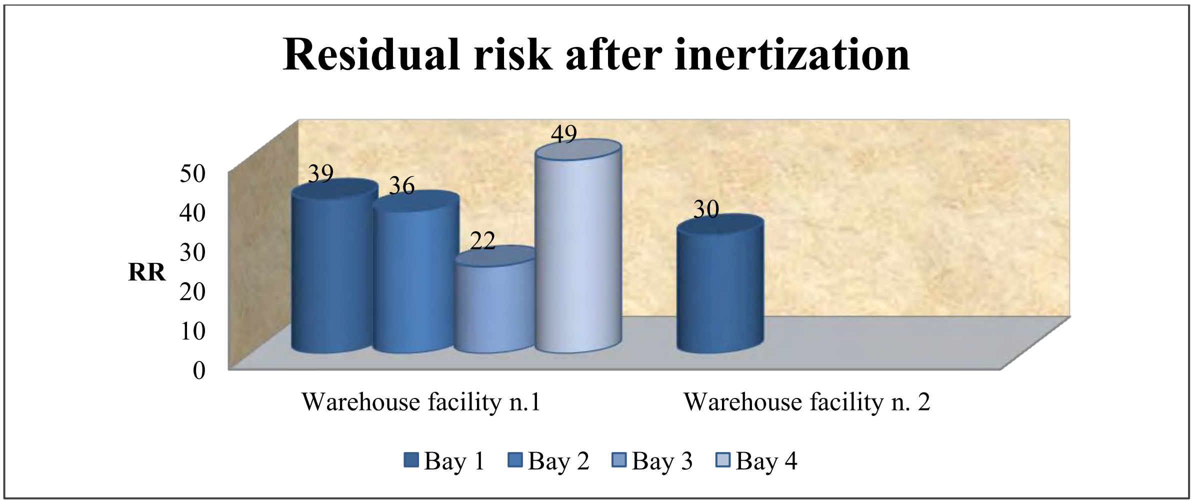


Fig. 6.1.5.1: *Residual risk after tank's inertization.*

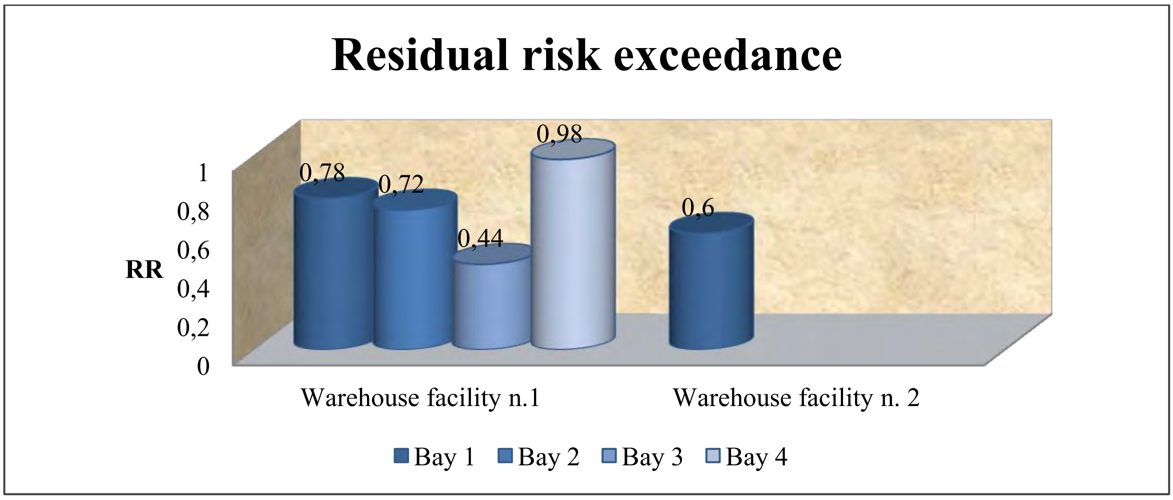


Fig. 6.1.5.2: *Risk threshold value exceedance.*

6.2 Risk comparison

It can be seen, recalling the Machinery Directive 2006/42/CE, the residual risk decrease to a value below the limit value of all process tanks located in the production area, thus classifying them in a MEDIUM level of risk as it can be seen in Fig. 6.2.1.

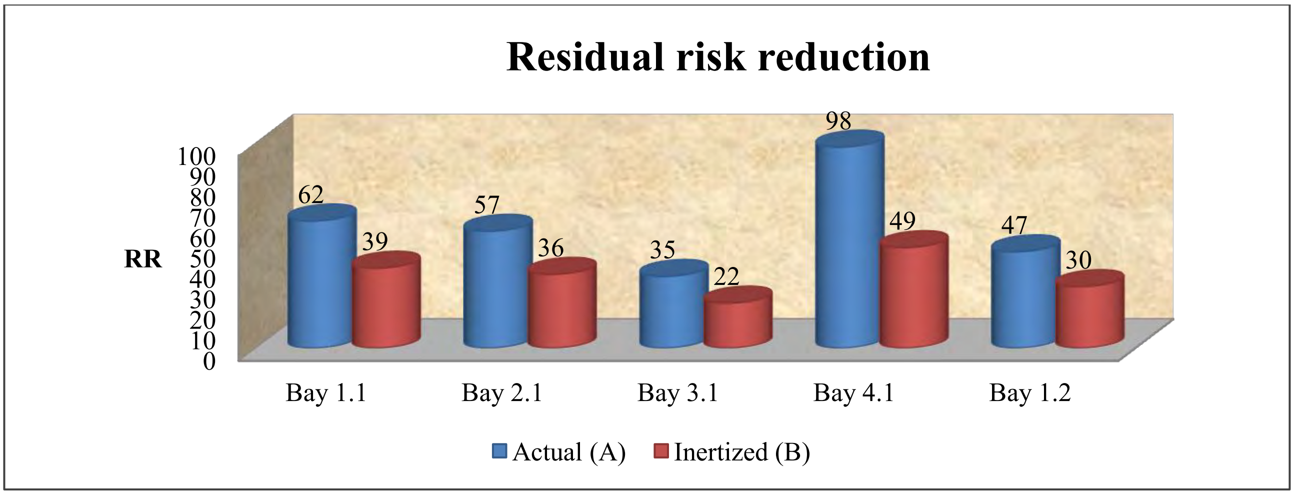


Fig. 6.2.1: *Residual risk reduction.*

6.3 Classification of areas at risk of explosion

Recalling Chapter n.2 (Classification of areas at risk of explosion, 2.3.1) in this paragraph a new classification of areas at risk of explosion is done, adopting inerting systems. Both the guideline CEI 31-35 CEI 31-56 are focused particularly on the consequences that inerting can have in the classification of areas at risk of explosion on the outside of the compartment inert. It thus defines the inerting system availability through the following descriptors:

- Availability GOOD. The inerting available continuously;
- Availability ADEQUATE. The inerting is available during normal operation. Interruptions are permitted provided they are infrequent and of short duration;
- Availability POOR: inerting does not meet the availability requirements or GOOD ADEQUATE, although there are no breaks for long periods.

The availability GOOD is obtaines through the redundancy of inerting systems or with technical measures that prevent the emission sources in the event of absence of inerting. The influence of the inertization system on the areas outside the containment protected is given by the following Tab. 6.3.1:

Tab. 6.3.1 : *Influence of inerting systems on the types of zones.*

DEGREE OF EMISSION WITHOUT INERTIZATION	**AVAILABILITY OF INERTING SERVICE**					
	Good		**Appropriate**		**Poor**	
Continuous	(Zone 2NE) (Gas,vapors, mists)	(Zone 22NE) (Combustible dust)	Zone 1 (Gas,vapors, mists)	Zone 21 (Combustible dust)	Zone 0 (Gas,vapors, mists)	Zone 20 (Combustible dust)
First	Not-hazardous area		Zone 2 (Gas, vapors, mists)	Zone 22 (Combustible dust)	Zone 1 (Gas, vapors, mists)	Zone 21 (Combustible dust)
Second	Not-hazardous area		Not-hazardous area		Zone 2	Zone 22

			(Gas, vapors, mists)	(Combustible dust)

Assuming the redundancy of the inerting systems, as is seen from Table 6.3.1, the area previously classified as area 0, now is classified as area 2, that is an area which an explosive atmosphere due to the presence of gas is not likely to be present during normal operation but, if this is done, it is possible to persist only for short periods. On the other hand, the area surrounding the process reactors, previously classified as Zone 1, through inerting, it becomes a not-hazardous area. The guideline also provides a series of recommendations on actions to be taken in cases where inerting fails. In general the planned interventions will be of three types, and speed request from the action will be a function of the category of the equipment and the potential danger zone that takes place in the absence of containment. The procedures provided for cover the following aspects:

- Presence of optical-acoustic alarms;
- Actions aimed at restoring the efficiency inerting;
- Decommissioning of equipment (electric and non-electric).

The Tab. 6.3.2 is a summary of the actions to be performed.

Tab. 6.3.2 *Measures to be taken in the event of interruption of the inerting system.*

Type of zone in the absence of depression	**Equipment classification in accordance with Directive 94/9 / EC**		
	II 2D	**II 3D**	**Not suitable for hazardous areas**
Zone 1 (Gas, vapors, mists) Zone 21 (Combustible dust)	No action	1) Visual and audible alarm; 2) Immediate action to restore inerting; 3) Equipment automatic disconnecting.	1) Visual and audible alarm; 2) Immediate action to restore inerting; 3) Equipment automatic disconnecting.
Zone 2 (Gas, vapors, mists) Zone 22 (Combustible dust)	No action	No action	1) Visual and audible alarm; 2) Immediate action to restore inerting; 3) Equipment automatic disconnecting.

All systems with inert environment must carry the following sign:

ATTENTION - PROTECTED CONTAINER WITH INERTING

They will also be provided with written instructions for use and maintenance. In this regard, the CEN/TR 15281 indicates that the manufacturer of the inerting is required to supply the following information:

- Definition of the operating limits of use (substances, temperatures, pressures);
- Conditions of supply of the inert gas (oxygen, concentration, storage, flows);
- Checks and maintenance required to ensure the system for leaks;
- Requirements for the regular maintenance, calibration and monitoring system;
- Protective equipment;
- Controls on changes or replacements of process equipment;
- Details of the recordings from the original design, the changes, process changes and calibrations.

6.4 The risk to the health of workers

A possible reduction in the percentage of oxygen in the air can cause death in a few seconds. In this regard, the effects of oxygen concentration on human life are reported in Tab.. In Europe, it was proposed the classification of areas at risk of asphyxia ("Johnson, 2008") (Tab. 6.4.2) according to the criteria of near-field and far-field, already applied to the release of poison gas. The descriptors of these areas are summarized in Tab. 6.4.1.

Tab. 6.4.1: *Effects of oxygen concentration on human life.*

Oxygen percentage (vol)	Effects and syntoms
23,5	Maximum level of security. 23% is the level of alarm for many oxygen sensors on the market.
21	Typical oxygen concentration.
19,5	minimum security level. 19% is the level of alarm for many oxygen sensors on the market.
15-19	First signs of hypoxia. decreased ability to work. They can be induced symptoms particularly serious in people with coronary problems, lung and circulation. respiration increases with marked stress, tachycardia.
12-14	Respiration increases with stress, tachycardia, marked decrease of muscle coordination, perception. mental confusion.
10-12	It increases breathing speed and depth. Mental confusion. Blue lips.
8-10	Nausea, vomiting, fainting. unconsciousness. ashen face. blue lips.
6-8	6 minutes - 50% chance of death. 8 minutes - 100% chance of death.
4-6	Coma in 40 seconds, convulsions. cessation of breathing. Death.

Tab. 6.4.2: *Definition of zones of asphyxiation.*

Zone type	Description	Examples
30	Area is present continuously or for long periods or frequently atmosphere to limited oxygen content (suffocating).	This condition is typical of the interior of the containment inert.
31	Area in which an atmosphere in limited oxygen content (asphyxiating) is likely to occur occasionally during normal activities.	This pattern can be found in the areas of access to confined spaces and inert.
32	Area in which during normal activities is not likely to form an atmosphere in limited oxygen content (asphyxiating) or, quallora it does occur, only short-term.	The situation may occur in the vicinity of the piping and containment process placed indoors.

At the end of the classification of areas of asphyxiation it proceeds, as in the case of the classification of areas ATEX, the graphic description of the results of classification. However, the classification of areas of asphyxiation is not provided in any Community rule.

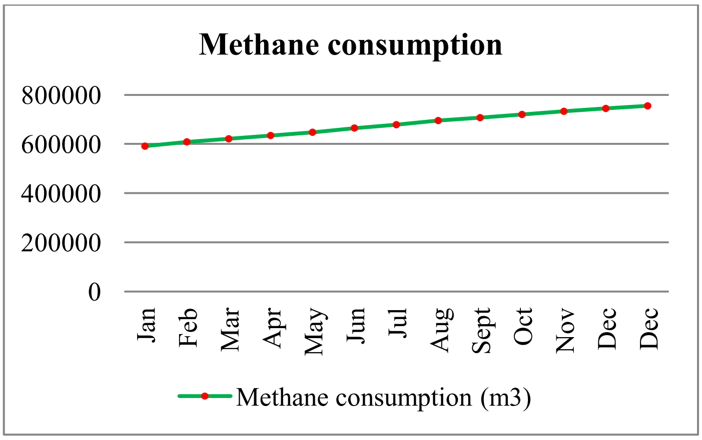
Chapter 7. Costs – Benefits analysis

The cost-benefit analysis is carried out with the aim of quantifying, assessing and comparig the costs and benefits that the three solutions A, B, C offer. Such analysis is fundamental to understand, currently, the most advantageous, in terms of costs, safety and environmental protection.

7.1 Aspiration plant consumption and mantainance costs (Scenario A)

The aspiration system conveys the vapors suction from the tanks to a post-combustor which, fueled by methane, is active on average 282 days per year, daily 13 hours and 10 minutes. The data relating to the air flow rates and the operation of the afterburner are reported in Fig. 7.1.1:

Tab. 7.1.1: *Methane consumption, year 2014.*



Through the MAX function, it has been calculated the maximum value of the data set already shown and costs estimation reported in Tab. 7.1.1:

Tab. 7.1.1: *Methane consumption 2014, at flowrate of 30.000 Nm^3/h.*

Current methane consumption, 2014	
Methane consumption	208,014 m^3
Cost	0,53 €/m^3
Methane consumption costs	**110,247 €**

Based on the increase of air flow rate expected for the end of the current year 2015, the total cost of the consumption of natural gas and electricity is as follows:

Tab. 7.1.2: *Methane consumption 2014, at flowrate of 30.000 Nm^3/h.*

Methane consumption expectations, 2016	
Methane consumption	374,425 m^3
Cost	0,53 €/m^3
Methane consumption costs	**198,445 €**

The fans, governing the apiration pipeline, are activated on demand during the production processes. Systems operating time is reported as follows (Tab. 7.1.2):

Tab. 7.1.3: *Systems operating time.*

Operating time

	Day/year	Hours/day	Hours/year
Post-combustor	282	11	3,102
Aspiration plant 1	282	10	2,820
Aspiration plant 2	282	10	2,820

Electrical energy has been estimated according to operating time, power and electrical energy cost verified on 2015, June 14, of 0,16 €/kWh (Tab. 7.1.3). Knowing that Electricity cost is calculated according to the following equation:

$$Electricity\ cost = Power\ (kWh) * Operating\ time\ (h) * Electrical\ energy\ cost\ (\frac{€}{\mathrm{kWh}})$$

Tab. 7.1.4: *Electrical energy consumption.*

	Power	Electrical energy cost	Yearly costs
Post-combustor	200 kW	0,16 €/kWh	99,264 €
Aspiration plant 1	224 kW		101,069 €
Aspiration plant 2	113 kW		50,985 €

Tab. 7.1.5: *Aspiration plant costs economic balance.*

Costs estimation	
Annual aspiration plant electrical energy	251,318 €
Annual methane consumption	198,445 €
Annual aspiration plant maintainance	8.000 €
Every 10 years, thermal oxidizer's ceramic beds substitution and disposal	100.000 €
Every 5 years, bag filters mantainance	40.000 €

Tab. 7.1.3: *Aspiration plant, 10 years economic balance,*

Consumption and mantainance	**4,757,630 €**

7.2 Inertization application costs (Scenario B)

In order to quantify the cost of applying blanketing solution to the process tanks, it was conducted an approximate economic balance based on the total quantity of ink produced in 2014, then the estimated process losses and the number of emptying and filling of the tanks during the production phase; for losses quantification, reference is made to Chapter 5.11.6, while for ink production, reference is made to Chapter 5.11.2. To give an initial estimation of costs for inerting of tanks, it has been consulted the SIAD Company, leader in the production and marketing of the entire range of industrial gases.

7.2.1 Inertization plant using Nitrogen (N_2)

The nitrogen, typically provided in liquid phase, it is stored in cryogenic containers insulated vacuum, and kept at very low temperatures (-196 ° C): the tanks are equipped with level controls and pressure with remote sensing (optional) for automatic reordering of the product. The nitrogen liquid in the cryogenic tank, is gasified in suitable atmospheric evaporators the desired pressure and between ~ 2:12 barg. The inertisation plant will consist of one cryogenic storage of liquid nitrogen, to a vaporizer capable of delivering up to 120 Nm3 / h of nitrogen gas and by the control devices and safety. The title of liquid nitrogen and 99.95%. The cryogenic tank and the vaporization systems are materials provided on loan of use, throughout the period of contract of purchase by SIAD product liquid nitrogen. The nitrogen gas will be reduced to a pressure $P1 \leq 5$ bar from the first stage reducer mounted on the first section line of transportation of nitrogen gas. The

reducers of stage II will further reduce the pressure to P2 equal to about 20 mbar and feed the three groups of tanks containing the different solvents while maintaining the interior of the storage an inert atmosphere and free of moisture. In the loading phase of the solvents, the double-acting valves will discharge the mixture nitrogen and vapors solvents into the atmosphere if within the limits of law; otherwise you'll have to direct them to provide an appropriate abatement system (eg through a closed circuit for their recovery, or starting them at Vs. combustor). For the storage and dispensing of liquid nitrogen will put at disposal, such as material loaned for use, n ° 1 cryogenic container from 6,000 l, complete with suitable evaporator air pollution. Liquid nitrogen necessary for the operation of the proposed plant will be provided with the following
economic conditions:

Tab. 7.2.1.1: *Nitrogen inertization plant: installation and service cost.*

	Yearly balance	**10 year balance**
Price of materials	249,960 €	/
Yearly charge service	3.000 €	30.000 €
Transport charge	1.800 €	18.000 €
Cost of total Sm^3 of nitrogen	21.044 €	210.445 €
Overall cost	275,804 €	**2,758,045 €**

7.2.2 Nitrogen self-production

Compared to traditional ways of supplying, there are no hidden costs with nitrogen self-production generator: the only raw materials it uses are air and electricity, in quantities which depend on the output required. CLAIND company has been selected as a suitable supplier of a nitrogen self-production system.
The company offers a series of products and services designed to fulfill essential requirements associated with hydrogen, nitrogen and zero air. The CLAIND solution for self-production of nitrogen makes use of Pressure Swing Adsorption technology (PSA), which, through the use of specially selected molecular sieves (CMS), makes it possible to obtain extremely pure nitrogen (up to 99.999%) at very moderate cost. Pressure Swing Adsorption (PSA) uses, in most cases, two vessels, packed with carbon molecular sieve (CMS). The CMS adsorbs Oxygen as compressed air flows upward through one of the vessels while the other vessel is depressurized and a small amount of the nitrogen output is flowing downward (counter flow) to drive off or desorbs the oxygen and moisture collected by the vessel when it was online removing oxygen from the air. The vessels alternate this adsorption and desorption process. There are several steps in the process; equalization, pressurization/depressurization, adsorption/purge, then back to equalization. This is a basic description of the process, but there are several things happening at various times throughout the time cycle which is generally a 2 minute cycle total.

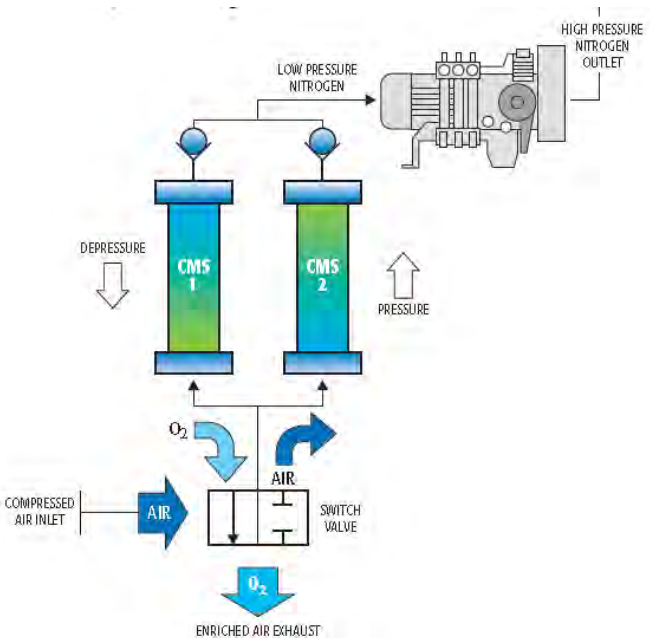


Fig. 7.2.2.1: *Self-production technology flowsheet.*

Tab. 7.2.2.1 below compares a high flow, low purity membrane (HFLP), a high purity lower flow membrane (HPLF) and pressure swing adsorption (PSA) type nitrogen generators. In the table there are some abbreviations that need to be defined here. SCFM N_2 is an arbitrary flow rate used for the basis of these examples. SCFM is nitrogen and air flow at atmospheric conditions that the nitrogen and the compressed air manufacturers use as their standards. Multiply this number by the N_2 SCFM to get the SCFM Air required. CCF is the Compressor Correction Factor. Size the compressor 1.25-1.3 times the required compressed air SCFM to allow for winter/summer ambient, variations in membrane performance, flow unit conversion, as well as the compressor manufacturer's flow tolerance.

Tab. 7.2.2.1: *Effects of purity selection on energy required.*

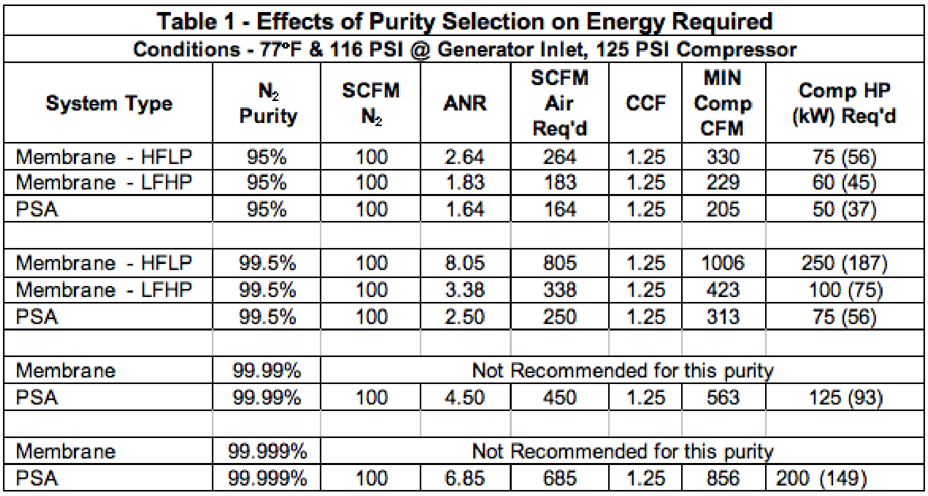


Table 1 - Effects of Purity Selection on Energy Required

Conditions - 77°F & 116 PSI @ Generator Inlet, 125 PSI Compressor

System Type	N_2 Purity	SCFM N_2	ANR	SCFM Air Req'd	CCF	MIN Comp CFM	Comp HP (kW) Req'd
Membrane - HFLP	95%	100	2.64	264	1.25	330	75 (56)
Membrane - LFHP	95%	100	1.83	183	1.25	229	60 (45)
PSA	95%	100	1.64	164	1.25	205	50 (37)
Membrane - HFLP	99.5%	100	8.05	805	1.25	1006	250 (187)
Membrane - LFHP	99.5%	100	3.38	338	1.25	423	100 (75)
PSA	99.5%	100	2.50	250	1.25	313	75 (56)
Membrane	99.99%	Not Recommended for this purity					
PSA	99.99%	100	4.50	450	1.25	563	125 (93)
Membrane	99.999%	Not Recommended for this purity					
PSA	99.999%	100	6.85	685	1.25	856	200 (149)

Pressure of air inlet is a parameter involved in energy requirement. By raising the pressure, smaller systems could be utilized to save on capital costs for the nitrogen generator, but the compressor will usually go to the next compressor HP size by going from a 125 PSI to a 150 PSI compressor. In general, the compressed air industry has used a "rule of thumb" of 1% kW increase for every 2 PSI increase. Finally, the purity has a not less important weight. The higher the percent nitrogen required, the larger the system to obtain a given flow rate. More compressed air will be required and more electricity consumed. Capital cost, long term maintenance cost, and floor space will increase as well. Whereas, a 95% N2 system will take approximately 2 SCFM of compressed air for 1 SCFM of nitrogen, the ratio of air to nitrogen could be as high as 12:1 at 99.999% N2 in some older systems. Here are a few "Rule of Thumb" Nitrogen species for some industries (For Comparison Only):

1. Blanketing to prevent hazardous conditions – Approximately 95-97% for most applications;
2. Blanketing edible vegetable oils – approximately 99.9%;
3. Food Packaging – approximately 99.5% for most applications;
4. Printed Circuit Boards – Traditionally has been in the 99.9%+ range, but long term testing shows that this application can be done at 97% with no visible or long term effects;
5. Heat treating metals – Depending on materials and process, can be 97% to as High as 99.999% (10 PPM of O2).

Over the life of the equipment, approximately 90% of its life costs will be in the energy required to run it. Capital costs, installation and maintenance costs are small compared to the power consumption. That is why it is so important to make wise decisions on your nitrogen equipment selections. That is why it is so important to make wise decisions on the necessary nitrogen equipment selections.

7.2.3 Inertization plant using Carbon Dioxide

The carbon dioxide, supplied in liquid phase, and stored in cryogenic containers insulated vacuum, and maintained at temperatures of -20 ° C at a pressure of about 18 bar. The tanks are equipped with level controls with remote sensing and pressure (optional) for the automatic reordering the product. The liquid carbon dioxide, contained in the cryogenic tank, is gasified in suitable evaporators atmospheric to the desired pressure and between ~ 2:08 barg. The inertisation plant will consist of one cryogenic storage of liquid carbon dioxide, from a vaporizer capable of delivering up to 50 Nm^3 / h of gaseous carbon dioxide and the control devices and safety. The cryogenic tank and the vaporization systems are materials provided on loan of use, throughout the period of contract of purchase of the product by SIAD carbon dioxide. The carbon dioxide will be reduced to a pressure $P1 \leq 5$ bar from the first stage reducer mounted on the first section of the line of transport of carbon dioxide. For the storage and dispensing of liquid carbon dioxide will put at disposal, such as material loaned for use, one cryogenic container of 6.000 l, complete with suitable evaporator. Liquid carbon dioxide necessary for the operation of the proposed plant will be provided with the following economic conditions.

Tab. 7.2.3.1: *Carbon Dioxide inertization plant: installation and service cost.*

	Yearly balance	**10 year balance**
Price of materials	390,000 €	/
Yearly charge service	3.000 €	30.000 €
Transport charge	1.800 €	18.000 €
Cost of total Kg of CO_2	15.587 €	155.870 €
Overall cost	410,387 €	**4,103,870** €

7.3 Rotary concentrator costs (Scenario C)

As mentioned in Chapter 1, scenario B includes the installation of the concentrator, for polluted air with a high concentration of solvent. It is therefore expected, the installation of a new filter, a new fan and a rotary concentrator that will be capable of self support combustion in the after-burner (Fig. 7.3.1 and 7.3.2). The flow of air is reduced from the input stream of 54,000 Nm^3 / h of air to one output of 7,000 Nm^3 / h having a high concentration of solvent.

Fig.7.3.1: *Rotoconcentrator.*

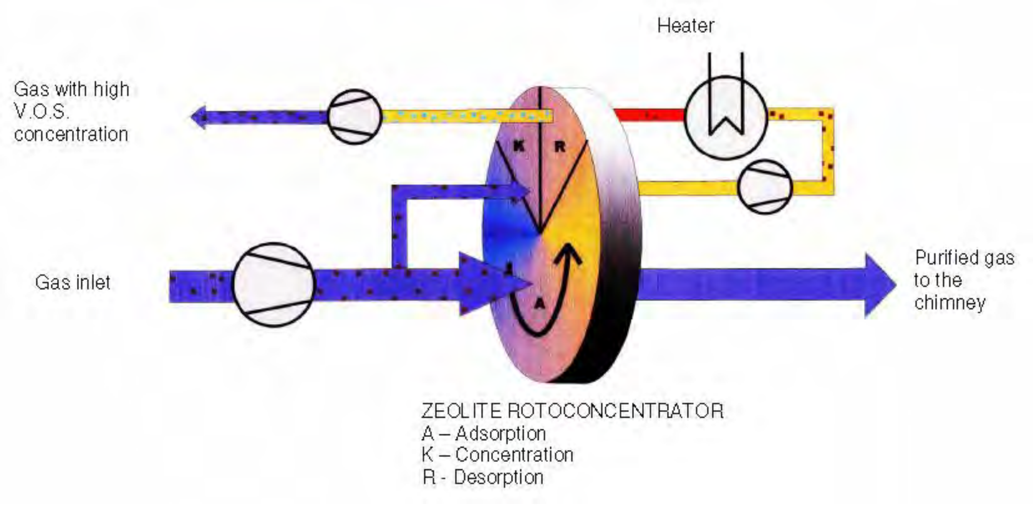


Fig. 7.3.2: *Rotoconcentrator: operating principles.*

Management and maintenance costs of scenario C are shown in Tab. 8.1:

Tab. 8.1: *Rotary concentrator yearly economic balance.*

Installation and Management	1,800,000 €
Electrical Energy Consumption	219,054 €
Methane Consumption	10,000 €
Every 5 years Rotoconcentratore Substitution	280,000 €
Yearly maintainance	20,000 €
Every 5 years, bag filters substitution	40,000 €

Tab. 8.2: *Rotary concentrator costs, 10 years economic balance.*

Installation and management	1.800.000 €
Consumption and maintainance	3,130,540 €
	4,930,540 €

7.3 Energetics benefits and Environmental benefits

7.3.1 Energetics benefits

It was previously introduced the benefits that the adoption of the inerting process involves the entire plant. It is shown, in practice, that it reduce fire and explosion risk, in fact eliminating the explosive atmosphere due to the presence of combustion air at the liquid-vapor; from the energy point of view this application translates the shutting down of the post-combustor and two possible ways to treat the aspiration gases, downstream the filters, during the stages of powder loading. This, can be done by the mean of two possible systems:

1. Cryogenic condensation with liquid nitrogen;
2. Adsorption on activated carbon with nitrogen regeneration.

Applying these two possible systems, they cancel therefore the costs related to the use of natural gas and electricity used for the operation of the suction system and the after-burner itself.

7.3.1.1 FREEZE-FLO: the cryogenic system for the removal of volatile off-gases

FREEZE-FLO is the result of research, know-how and SIAD experience in cryocondensation technology, it is is designed and realized "ad hoc" to purify small and medium gas flows, in the field of flow rates between 0 and 100Nm3 / h. The process of cryogenic condensation is based on the possibility to cool the gaseous effluents polluted by volatile organic compounds (VOCs) at very low temperatures, of the order of -100 ° C, using the liquid nitrogen as energy source. The separation of the pollutants is obtained thanks to the drastic reduction of the vapor pressure at the equilibrium values of the liquid / vapor or solid / vapor made to minimum temperatures reached by cryogenic. It is therefore possible to condense and "recover" as many organic pollutants present in the gaseous stream, widely used in many areas of industrial production. The special conformation of the heat exchangers in indirect nitrogen flow, in countercurrent with the stream polluted, having large heat exchange surface, favors the formation and evacuation of the condensate, which is collected in a dedicated tank, or retrieved directly inside the reactors by it comes from. The format adopted for "indirect cooling" also allows to reuse the nitrogen flow exiting the column rio condensation such as inerting agent: it is the case of reactors, mixers process and storage tanks so properly equipped to the environment and operational safety. Flow rate and pressure of the nitrogen and outlet temperatures of the various streams are the main parameters for measurement and control: operations and settings are provided in manual or automatic. If tratment flows are more than 100 Nm^3 / h, SIAD has other system solutions based on the same technology however condensation (Paragraph 7.3.1.2).

Fig. 7.3.1.1: *Freeze-Flo Plant.*

7.3.1.2 Adsorption on activated carbon with nitrogen regeneration.

SIAD has developed systems for adsorption / adsorption with active carbon (or other adsorbent materials) of emissions containing organic pollutants, using a new regeneration technique "beds" adsorption. This technique consists in heating with hot nitrogen in closed circuit, and in the subsequent desorption under vacuum, to achieve the removal of the adsorbed substances. The flow that is generated, of modest volumetric flow rate (about 1 ÷ 2% that of the treated flow) but saturated with the substances desorbed, is sent to a cryogenic condenser in which these substances are separated and recovered. Thanks to this technique, all the flows of the treatment plant, the treaty main flow and those produced during the regeneration treatment, are discharged into the atmosphere absolutely free of pollutants.

Fig. 7.3.1.2: *Adsortion plant.*

7.3.2 Environmental benefits

The application of the technique of inerting process tanks benefits, as we have seen, both from the point of view of the risk, the economic and energy; last but not least, the environmental one. The current system, from the environmental point of view, involves the operation of the thermal oxidizer that receives vapors from the working areas that, through the process of combustion, reduces the volatile organic substances allowing the company to comply with the legal limits set by Decree 152/2006 for emissions into the atmosphere. Sampling conducted by Ecoricerche comply with maximum projected emissions, but nevertheless contribute to air pollution annually. Thanks to the data provided by the same laboratory, it was possible to develope the following Tab. 7.4.1 containing the results of sampling carried out on 2014, Semptember 22. All results in concentration refer to the volume of dry effluent compared to normal physical conditions of 0C, 101.3 kPa and dry gas, average flow rate 24,600 Nm3/h; test methods are consistent with those provided by the Provincial Council resolution n. 173 of the 2012, May 22. The results obtained are derived from sampling continued for at least 60 minutes.

7.3.2.1 Aspiration system emissions

INPUT to the thermal oxidizer

Tab. 7.3.2.1: *Total substances Table D Class III.*

	Aspiration system

Compound	mg/Nm^3	g/h
n-esane	1,0	24,8
Tetrahydrofuran	0,51	12,4
Isobutyl alchool	0,10	2,5
1-methossi-2-propanol	1,8	44,4
Ethilbenzene	0,096	2,3
1-Methossi-2-propilacetate	0,46	11,2
Total substances class III	4,0	98

Tab. 7.3.2.2: *Total substances Table D Class IV.*

	Aspiration system	
Compound	**mg/Nm^3**	**g/h**
Methyl Acetate	0,44	10,7
Isopropyl Acetate	3,3	80
MethylEthylKethone	8,4	204
Isopropil Alchool	1,6	37,8
n-propylic Alcool	0,72	17,5
Toluene	4,2	102
Butyl Acetate	0,26	6,4
Xylenes	0,34	8,2
Total substances class IV	19,3	467

Tab. 7.3.2.3: *Total substances Table D Class V.*

	Aspiration system	
Compound	**mg/Nm^3**	**g/h**
n-heptane	1,8	44,4
Acetone	1,2	28,6
Ethyl Acetate	1.711	41.406
Ethanol	87	2.113
Other organic substances espressed as n-heptane	8,5	206
Total substances class IV	1.810	43.798

OUTPUT of the thermal oxidizer

The values shown in Tab. 7.4.2.1 are experimental values measured at the chimney referred to the current intake aspiration system. The yield abatement of the post-combustor is approximately 98%.

Tab. 7.3.2.4: *Total substances Table D Class III: comparison between the two systems.*

	Aspiration system		
	mg/Nm^3	**g/h**	**Kg/year**
Total substances Table A1 Class III	<0,091	<2,2	/
Substances Table C Class V			/
Nitrogen oxydes (Horiba)	0,22	71	262
Total substances Table C Class V	2,9	71	262
Total substances Table D Class II	0,2	<4,9	
Total substances Table D Class III	0,27	<6,6	
Substances Table D Class IV			
Methyl Ethyl Ketone	0,11	2,8	10
Toluene	0,077	1,9	7
Total Substances Table D Class IV	0,19	4,7	17
Substances Table D Class V			
Ethyl Acetate	22,3	548	2.024

Ethanol	2,6	64	236
Other organic substances espresse as heptane	0,19	4,7	17
Total Substances Table D Class V	25,1	617	2.279
Total organic carbon	22,8	561	2.072
Carbon Monoxide (HORIBA)	129	3.181	11.751

Tab. 7.3.2.5: *Comparison with limits referred to test report.*

	Aspiration system	**Limit value**
	mg/Nm^3	**(mg/Nm^3)**
Total Organic Carbon	22,8	40
Carbon Monoxide (Horiba)	129	295
Substances Table A1 Class III	<0,091	754
Substances Table C Class V	2,9	140
Substances Table D Class II	<0,20	65
Substances Table D Class II+III	<0,47	377
Substances of Table D Class II+III+IV	0,66	24
Substances of Table D Class II+III+IV+V	25,8	3

Tab. 7.3.2.6: *Dust comparison with limits referred to test report.*

	Aspiration system			**Regulatory limit**
	mg/m^3	Kg/y	g/h	(mg/Nm^3)
Total dust	0,22	0,4	0,11	20

As can be seen from the tables above, the vapors leaving the afterburner are in accordance with the legal limits during each sampling. Fig. 7.4.1 gives a visual idea of emission quantities for each compound.

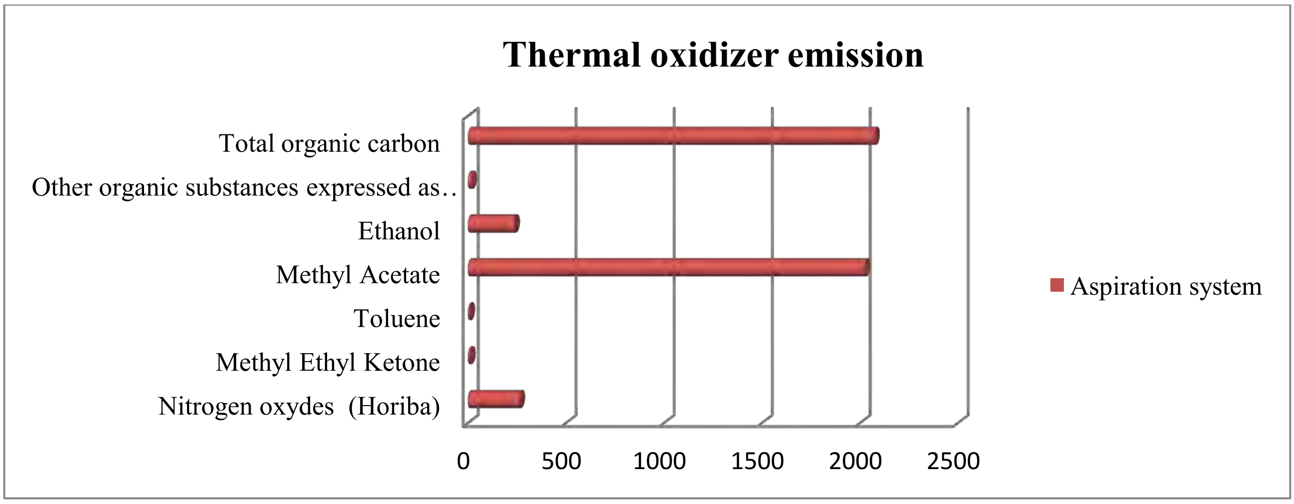


Fig. 7.3.2.1: *Emissions reduction: comparison between the two considered preventive measures.*

As explained earlier, the inerting process, following the shutdown of the afterburner, eliminates annual emissions of gaseous pollutants. Through the cryogenic condenser can be the liquefaction of the gaseous effluent and the recovery of solvent at the same time to the regeneration of inert gas.

Chapter 8. Final evaluation and conclusions

In the first chapter, it is exposed the problematic to understand what is among the three solutions A, B and C under the best profile:

- Economic;
- Risk;
- Environmental.

From an environmental and fire hazards point of view, scenarios A and B are equal; scenario C, however, improves the current situation, both in terms of risk (Chapter 6), environmental and economic (Chapter7). At this point, it is therefore reasonable to compare the three scenarios to choose and implement what, more improves the three profiles previously reported (Fig. 8.1).

	Scenario A Aspiration System	**Scenario B Blanketing**	**Scenario C Rotary Concentrator**
Economic	XX	XXX	X
Risk	X	XX	X
Environemntal & Energetics	X	XX	X

Fig: 8.1: *Scenario Assessment.*

As can be seen from Fig. 8.1, the scenario C from an economic, environmental and fire risk profile, is the most beneficial one and which can only improve the business environment, the health of workers, and reduce the annual management costs that may reflect an improvement in production margins.

ANNEX A

Risk
Assessment

ANNEX A. Risk Assessment

1.1 Warehouse facility n.2, bay 1

Surface area	**1.489,6**
δ_{q1}	1,40
δ_{q2}	1,20
$\delta_n = \prod_i \delta_{ni}$	0,26
Specific fire loading rate (nominal) qf	3.410 Kg wood/m^2
Specific fire loading rate of design qf,d	1.489,6 Kg wood/m^2
Class fire	240

Multiplying factors of risk		
PARAMETER	**DEFINITION**	**VALUE**
Burning rate	R_c	1,5
Toxicity of the combustion products	P_f	2
Probability of initiation	Pi	2,2
Probability of personal injury	P_{aff}	1

$$F_c = 1 - \frac{D_{ok}}{N_{tot}}$$

Dove:

- D_{ok} = Number of questions with an affermative answer = 193
- N_{tot} = Total number of questions to answer than "QUESTION IS NOT APPLICABLE TO THE SECTOR UNDER CONSIDERATION"= 196

$$F_c = 1 - \frac{193}{196} = 0,1$$

$$RR = 1.489,6 * 1,5 * 2 * 1,6 * 1 * 0,05 = 476,5$$

Since RR > 50, as first defined the area is characterized as HIGH RESIDUAL RISK.

1.2 Warehouse facility n.2, bay 2

Surface area	**1.469,6**
δ_{q1}	1,40
δ_{q2}	1,20
$\delta_n = \prod_i \delta_{ni}$	0,26
Specific fire loading rate (nominal) qf	250 Kg wood/m^2
Specific fire loading rate of design qf,d	109,4 Kg wood/m^2
Class fire	240

Multiplying factors of risk		
PARAMETER	**DEFINITION**	**VALUE**

Burning rate	R_c	1,5
Toxicity of the combustion products	P_f	2
Probability of initiation	Pi	1,6
Probability of personal injury	P_{aff}	1

$$F_c = 1 - \frac{D_{ok}}{N_{tot}}$$

Dove:

- D_{ok} = Number of questions with an affermative answer = 193
- N_{tot} = Total number of questions to answer than "QUESTION IS NOT APPLICABLE TO THE SECTOR UNDER CONSIDERATION"= 196

$$F_c = 1 - \frac{193}{196} = 0{,}005$$

$$RR = 109{,}4 * 2 * 2 * 1{,}6 * 1 * 0{,}01 = 35$$

Since RR > 50, as first defined the area is characterized as HIGH RESIDUAL RISK.

1.3 Warehouse facility n.2, bay 3

Surface area	**1.489,6**
δ_{q1}	1,40
δ_{q2}	1,20
$\delta_n = \prod_i \delta_{ni}$	0,26
Specific fire loading rate (nominal) qf	555 Kg wood/m^2
Specific fire loading rate of design qf,d	242,4 Kg wood/m^2
Class fire	240

Multiplying factors of risk		
PARAMETER	**DEFINITION**	**VALUE**
Burning rate	R_c	1,5
Toxicity of the combustion products	P_f	2
Probability of initiation	Pi	1,6
Probability of personal injury	P_{aff}	1

$$F_c = 1 - \frac{D_{ok}}{N_{tot}}$$

Dove:

- D_{ok} = Number of questions with an affermative answer = 193
- N_{tot} = Total number of questions to answer than "QUESTION IS NOT APPLICABLE TO THE SECTOR UNDER CONSIDERATION"= 196

$$F_c = 1 - \frac{193}{196} = 0{,}1$$

$$RR = 242{,}4 * 1{,}5 * 2 * 1{,}6 * 1 * 0{,}01 = 77{,}5$$

Since RR > 50, as first defined the area is characterized as HIGH RESIDUAL RISK.

1.4 Warehouse facility n.2, bay 4

Surface area	**1.469,6**
δ_{q1}	1,40
δ_{q2}	1,20
$\delta_n = \prod_i \delta_{ni}$	0,26
Specific fire loading rate (nominal) qf	751 Kg wood/m^2
Specific fire loading rate of design qf,d	328 Kg wood/m^2
Class fire	240

Multiplying factors of risk		
PARAMETER	**DEFINITION**	**VALUE**
Burning rate	R_c	1,5
Toxicity of the combustion products	P_f	2
Probability of initiation	Pi	1,6
Probability of personal injury	P_{aff}	1

$$F_c = 1 - \frac{D_{ok}}{N_{tot}}$$

Dove:

- D_{ok} = Number of questions with an affermative answer = 193
- N_{tot} = Total number of questions to answer than "QUESTION IS NOT APPLICABLE TO THE SECTOR UNDER CONSIDERATION"= 196

$$F_c = 1 - \frac{193}{196} = 0{,}1$$

$$RR = 328 * 2 * 2 * 1{,}6 * 1 * 0{,}05 = 105$$

Since RR > 50, as first defined the area is characterized as HIGH RESIDUAL RISK.

1.5 Warehouse facility n.2, bay 5

Surface area	**1.447,2**
δ_{q1}	1,40
δ_{q2}	1,20
$\delta_n = \prod_i \delta_{ni}$	0,26
Specific fire loading rate (nominal) qf	601,5 Kg wood/m^2

Specific fire loading rate of design qf,d	262,7 Kg wood/m^2
Class fire	240

Multiplying factors of risk		
PARAMETER	**DEFINITION**	**VALUE**
Burning rate	R_c	1,5
Toxicity of the combustion products	P_f	2
Probability of initiation	Pi	1,6
Probability of personal injury	P_{aff}	1

$$F_c = 1 - \frac{D_{ok}}{N_{tot}}$$

Dove:

- D_{ok} = Number of questions with an affermative answer = 193
- N_{tot} = Total number of questions to answer than "QUESTION IS NOT APPLICABLE TO THE SECTOR UNDER CONSIDERATION"= 196

$$F_c = 1 - \frac{193}{196} = 0{,}1$$

$$RR = 262{,}7 * 2 * 2 * 1{,}6 * 1 * 0{,}05 = 85$$

Since RR > 50, as first defined the area is characterized as HIGH RESIDUAL RISK.

1.6 Warehouse facility n.1, bay 1

Surface area	**530 m^2**
δ_{q1}	1,20
δ_{q2}	1,20
$\delta_n = \prod_i \delta_{ni}$	0,26
Specific fire loading rate (nominal) qf	433,7 Kg wood/m^2
Specific fire loading rate of design qf,d	162,4 Kg wood/m^2
Class fire	240

- D_{ok} = Number of questions with an affermative answer = 193
- N_{tot} = Total number of questions to answer than "QUESTION IS NOT APPLICABLE TO THE SECTOR UNDER CONSIDERATION"= 196

Multiplying factors of risk		
PARAMETER	**DEFINITION**	**VALUE**
Burning rate	R_c	1,5
Toxicity of the combustion products	P_f	2
Probability of initiation	Pi	2,2
Probability of personal injury	P_{aff}	1

$$F_c = 1 - \frac{216}{219} = 0{,}1$$

$$RR = RischioResiduo = 162{,}4 * 2 * 2 * 1{,}6 * 1 * 0{,}1 = 52$$

Since RR > 50, as first defined the area is characterized as HIGH RESIDUAL RISK.

1.7 Warehouse n.1, bay 2

Surface area	**550 m^2**
δ_{q1}	1,20
δ_{q2}	1,20
$\delta_n = \prod_i \delta_{ni}$	0,26
Specific fire loading rate (nominal) qf	397,2 Kg wood/m^2
Specific fire loading rate of design qf,d	148,7 Kg wood/m^2
Class fire	240

- D_{ok} = Number of questions with an affermative answer = 216
- N_{tot} = Total number of questions to answer than "QUESTION IS NOT APPLICABLE TO THE SECTOR UNDER CONSIDERATION"= 219

Multiplying factors of risk		
PARAMETER	**DEFINITION**	**VALUE**
Burning rate	R_c	1,5
Toxicity of the combustion products	P_f	2
Probability of initiation	Pi	2,2
Probability of personal injury	P_{aff}	1

$$F_c = 1 - \frac{216}{219} = 0{,}1$$

$$RR = RischioResiduo = 148{,}7 * 2 * 2 * 1{,}6 * 1 * 0{,}05 = 47{,}8$$

Since RR > 50, as first defined the area is characterized as HIGH RESIDUAL RISK.

1.8 Warehouse n.1, bay 3

Surface area	**510 m^2**
δ_{q1}	1,20
δ_{q2}	1,20
$\delta_n = \prod_i \delta_{ni}$	0,26
Specific fire loading rate (nominal) qf	244 Kg wood/m^2

Specific fire loading rate of design qf,d	91,4 Kg wood/m^2
Class fire	120

- D_{ok} = Number of questions with an affermative answer = 216
- N_{tot} = Total number of questions to answer than "QUESTION IS NOT APPLICABLE TO THE SECTOR UNDER CONSIDERATION"= 219

Multiplying factors of risk		
PARAMETER	**DEFINITION**	**VALUE**
Burning rate	R_c	1,5
Toxicity of the combustion products	P_f	2
Probability of initiation	Pi	2,2
Probability of personal injury	P_{aff}	1

$$F_c = 1 - \frac{216}{219} = 0{,}1$$

$$RR = 91{,}4 * 2 * 2 * 1{,}6 * 1 * 0{,}05 = 29{,}2$$

Since RR > 50, as first defined the area is characterized as HIGH RESIDUAL RISK.

1.9 Warehouse n.1, bay 4

Surface area	**1.455 m^2**
δ_{q1}	1,40
δ_{q2}	1,20
$\delta_n = \prod_i \delta_{ni}$	0,26
Specific fire loading rate (nominal) qf	589,7 MJ/m^2
Specific fire loading rate of design qf,d	257,6 Kg wood/m^2
Class fire	240

- D_{ok} = Number of questions with an affermative answer = 216
- N_{tot} = Total number of questions to answer than "QUESTION IS NOT APPLICABLE TO THE SECTOR UNDER CONSIDERATION"= 219

Multiplying factors of risk		
PARAMETER	**DEFINITION**	**VALUE**
Burning rate	R_c	2
Toxicity of the combustion products	P_f	2
Probability of initiation	Pi	1,6
Probability of personal injury	P_{aff}	1

$$F_c = 1 - \frac{216}{219} = 0{,}1$$

$$RR = 257{,}6 * 2 * 2 * 1{,}6 * 1 * 0{,}05 = 82$$

Since RR > 50, as first defined the area is characterized as HIGH RESIDUAL RISK.

ANNEX B

Tanks Volumes distribution and inks density

Tab. B.1: *Tank's volumes and ink's density.*

Machine	**Tank**	**Tank Volume (m^3)**	**Density of ink produced (t/m^3)**	**Max Liquid Volume (m^3)**	**Ullage Vapor space (m^3)**
Bay 1					
Drais 1	I1	6,9	0,909	5,5	1,4
	F1	6,9	0,909	5,5	1,4
Drais 2	I2	6,9	0,909	5,5	1,4
	F2	6,9	0,909	5,5	1,4
Drais 3	I3	6,9	0,909	5,5	1,4
	F3	6,9	0,909	5,5	1,4
Drais 4	I4	6,9	0,909	5,5	1,4
	F4	6,9	0,909	5,5	1,4
Drais 5	I5	6,9	0,909	5,5	1,4
	F5	6,9	0,909	5,5	1,4
M13	I6	11,1	72	4,5	2,2
	F6	8,2		5,3	2,5
D1	D1	11,1	113	8,8	4,2
Bay 2					
N10	I7	6,9	0,916	5,2	2,5
	F7	6,9	0,91	5,5	2,7
B11	D2	5	Variable	4	1
	D3	5	Variable	4	1
N9	I10	11,1	0,9	5	2,4
	F10	10	0,89	5,6	2,7
N8	I9	11,1	0,986	5	2,4
	F9	11,1	0,98	5	2,4
N12	I8	9	1,087	7,3	3,5
	F8/A	9,8	1,07	7,8	3,8
	F8/B	9,8	1,07	7,8	3,8
N6	I11	10,5	0,96	4,3	2,1
	F11	9,9	0,97	4,8	4,8
Bay 3					
N18	I27	7,1		4,2	2
	F35	8,2		4,8	2,4
	F36	8,2		4,8	2,4
N19	I26	7,1		3,2	1,5
	F33	8,2		3,6	1,7
	F34	8,2		3,6	1,7
N20	I28	7,1		4,2	2
	F37	8,2		4,8	2,4
	F38	8,2		4,8	2,4
Bay 4					
D5	D5	10,5		Variable	Variable
N10	I19	6		5,5	2,7
	F19	8		5,5	2,7
N14	I18	10,5	0,901	7,4	3,6
	F18	10	0,89	8	3,9
Bay 5					
M12	I20	50		31,3	15,1
	F20	50		37	17,8
	F21	15		12,5	6
Plant 2-Bay1					
D10	D10	23	287	20,4	9,8
D6	D6	11,7		9,2	4,4
D7	D7	11,7		9,2	4,4
F29	F29	6,5		5	1,5

F30	F30	6,5		5	1,5
F31	F31	6,5		5	1,5
F32	F32	6,5		5	1,5
N16	I24	11,7		10,9	5,3
	F24/A	12,8		10,6	5,2
	F24/B	12,8		10,6	5,2
N13	I23	11,7		9,42	4,5
	F23/A	12,5		10,4	4,8
	F23/B	12,8		10,4	4,8
N15	I22	11,7		9,6	4,6
	F22/A	12,8		10	4,8
	F22/B	12,8		10	4,8

ANNEX C

Inert gas requirements

Plant 1

MONOSOLVENT type inks, Bay 1

Tab. C.1: *Mixing reactors inert gas dosage.*

	YELLOW I21	RED I3	BLUE I4	BLACK I5	ORANGE I2	WHITE I6	D1	U.M.
N_{tot}	5,5	5,5	5,5	5,5	5,5	5,9	9,3	Nm^3

Tab. C.2: *Refining reactors inert gas dosage.*

	YELLOW F1	RED F3	BLUE F4	BLACK F5	ORANGE F2	WHITE F6	U.M.
N_{tot}	5,8/turnover	5,8/turnover	5,8/turnover	5,8/turnover	5,8/turnover	5,9/turnover	Nm^3

Tab. C.3: *Annual inert gas requirement.*

Ink	Number of turnover/output	Inert gas requirement/production	Total production in year 2014	Total Inert gas requirement
Drais1 YELLOW	2	22,6 Nm^3	26	**588 Nm^3**
Drais 4 BLUE	13	93 Nm^3	20	**1.860 Nm^3**
Drais 3 RED	15	93 Nm^3	17	**1.581 Nm^3**
Drais 5 BLACK	15	93 Nm^3	17	**1.581 Nm^3**
Drais 2 ORANGE	2	17 Nm^3	15	**2.551 Nm^3**
WHITE M13	2	18 Nm^3	72	**1.296 Nm^3**
D1	1	9,3 Nm^3	113	**1.051 Nm^3**

RASTER+ PROCESS type inks, Bay 2

Tab. C.4: *Mixing reactors inert gas dosage.*

	VIOLET 3 I11	GREEN 7 I10	RED I9	BLACK I8	VIOLET 23 I7	U.M.
N_{tot}	5,6	6,2	4,8	7,7	5,6	Nm^3

Tab. C.5: *Refining reactors inert gas dosage.*

	VIOLET 3 F11	GREEN 7 F10	RED F9	BLACK F8A/F8B	VIOLET 23 F7	U.M.
N_{tot}	5,9 /turnover	6,5/turnover	4,1/turnover	8,2/turnover	5,8/turnover	Nm^3

Tab. C.6: Dispersors inert gas dosage.

	D2	D3	U.M.
N_{tot}	4	**4**	Nm^3

Tab. C.7: *Annual inert gas requirement.*

	Number of turnover/output	**Inert gas requirement/production (Nm^3)**	**Total production in year 2014**	**Total inert gas requirement/year (Nm^3)**
N6 VIOLET3	9	59 Nm^3	27	**1.585 Nm^3**
N9 GREEN7	7	52 Nm^3	26	**1.352 Nm^3**
N8 RED	5	25 Nm^3	35	**875 Nm^3**
N12 BLACK	4	41 Nm^3	92	**3.772 Nm^3**
N10VIOLET23	13	81 Nm^3	15	**1.215 Nm^3**
D2	/	4 Nm^3	191	**764 Nm^3**
D3	/	4 Nm^3	173	**692 Nm^3**

PROCESS type inks, Bay 3

Tab. C.8: *Mixing reactors inert gas dosage.*

	YELLOW I27	**RED I26**	**BLUE I28**	**U.M.**
N_{tot}	4,8	4,5	4,8	Nm^3

Tab. C.9: *Refining reactors inert gas dosage.*

	YELLOW F35-F36	**RED F33-F34**	**BLUE F37-F38**	**U.M.**
N_{tot}	5,6/turnover	5,2/turnover	5,5/turnover	Nm^3

Tab. C.10: *Annual inert gas requirement.*

	Number of turnover/output	**Inert gas requirement/production**	**Total production in year 2014**	**Total inert gas requirement/year**
N18 YELLOW	5	33 Nm^3	167	**5.477 Nm^3**
N19 RED	9	52 Nm^3	102	**5.232 Nm^3**
N20 BLUE	5	33 Nm^3	129	**4.257 Nm^3**

PROCESS type inks and storage tanks, Bay 4

Tab. C.11: *Mixing reactors inert gas dosage.*

	BLACK I19	**BLUE I18**	**U.M.**
N_{tot}	4,5	4,8	Nm^3

Tab. C.12: *Refining reactors inert gas dosage.*

	BLACK F19	**RED/ORANGE F18**	**U.M.**
N_{tot}	4,5/turnover	4,8/turnover	Nm^3

Tab. C.13: *Annual inert gas requirement.*

	Number of turnover/output	Inert gas requirement/production	Total production in year 2014	Total Inert gas requirement
M 11 BLACK	2	27 Nm^3	15	**405 Nm^3**
N14 RED/ORANGE	5	24 Nm^3	44	**1.056 Nm^3**
D5	/	6,5 Nm^3	191	**1.242 Nm^3**

Tab. C.14: *Storage tanks inert gas dosage.*

	Storage tanks foundation for gravure			
	ST6	**ST5**	**ST4**	**D5**
N_{tot}	8,4 Nm^3	8,4 Nm^3	8,4 Nm^3	8

White Monosolvent, Bay 5

Tab. C.15: *Mixing reactors inert gas dosage.*

	WHITE I20	U.M.
N_{tot}	35,2	Nm^3

Tab. C.16: *Refining reactors inert gas dosage.*

	WHITE F20	WHITE F21	U.M.
N_{tot}	52,7/turnover	13/turnover	Nm^3

Tab. C.17: *Annual inert gas requirement.*

	Number of turnover/output	Inert gas requirement/production	Total production in year 2014	Total Inert gas requirement
M12 WHITE	2	153,7 Nm^3	72	**7.378 Nm^3**

Tab. C.18: *Storage tanks inert gas requirement.*

	Storage tanks foundation for gravure	
	ST7	**ST8**
N_{tot}	12 Nm^3	12 Nm^3

Plant 2

RASTER type inks, Bay 1

Tab. C.19: *Mixing reactors inert gas dosage.*

	YELLOW I23	RED I21	BLUE I22	U.M.
N_{tot}	11	10	9,9	Nm^3

Tab. C.20: *Refining reactors inert gas dosage.*

	YELLOW F24/A-F24B	**RED F22/A-F22/B**	**BLUE F23/A-F23/B**	**U.M.**
N_{tot}	10,7/turnover	10,4/turnover	10,9/turnover	Nm^3

Tab. C.21: *Dispersors inert gas dosage.*

	D10	**D6**	**D7**	**U.M.**
N_{tot}	21	9,7	9,7	Nm^3

Tab. C.22: C*olour’s mix.*

	F29	**F30**	**F31**	**F32**	**U.M.**
N_{tot}	5,3	5,3	5,3	5,3	Nm^3

Tab. C.23: *Annual inert gas requirement.*

	Number of turnover/output	**Inert gas requirement/production**	**Total production in year 2014**	**Total Inert gas requirement**
N13 BLUE	5	65 Nm^3	62	4.030 Nm^3
N16 YELLOW	5	65 Nm^3	77	5.005 Nm^3
N15 RED/ORANGE	11-13	146 Nm^3	54	7.884 Nm^3
F29	/	5,3 Nm^3	108	572 Nm^3
F30	/	5,3 Nm^3	68	360 Nm^3
F31	/	5,3 Nm^3	80	424 Nm^3
F32	/	5,3 Nm^3	36	191 Nm^3
D10	/	21 Nm^3	287	6.027 Nm^3
D6	/	9,7 Nm^3	222	2.153 Nm^3
D7	/	9,7 Nm^3	222	2.153 Nm^3

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