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Detergent, Bleach, Cleaner, and Sanitizer Applications

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Introduction

The ACL® brand of chlorinated isocyanurates are dry concentrated sources of chlorine for use in bleaches, detergents, cleaners and sanitizers. The ACLs® presently marketed are:

ACL56 ACL60 ACL90 PLUS

The numbers designate the approximate percentage of available chlorine in the particular product.

The ACL® chlorinated isocyanurates provide many benefits. The products are:

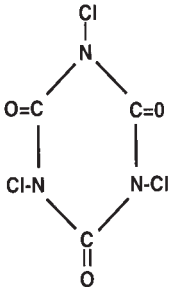
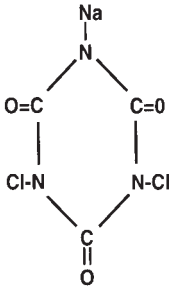
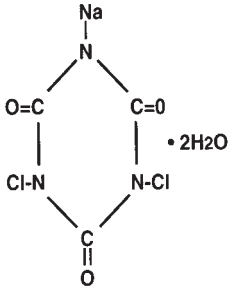
- soluble in water
- strong oxidizers, providing high levels of available chlorine which allow flexibility in formulation
- effective germicides in appropriate concentrations

The above characteristics have led to the use of ACL® in the following applications:

- laundry bleaches
- machine dishwash detergents
- cleaners and sanitizers
- cleansers

Introduction (continued)

Table 1* Physical and Chemical Properties of ACL® Chlorinated Isocyanurates

	ACL® 90 PLUS	ACL® 60	ACL® 56
Chemical Nomenclature	Trichloro-s-triazinetrione	Sodium dichloro-s-triazinetrione	Sodium dichloro-s-triazinetrione dihydrate
	Trichloro(iso) cyanuric acid	Sodium dichloro-(iso)cyanurate	Sodium dichloro-(iso)cyanurate dihydrate
	EPA No.: 935-37	EPA No.: 935-36	EPA No.: 935-38
	CAS No.: 87-90-1	CAS No.: 2893-78-9	CAS No.: 51580-86-0
Chemical Structure			
Formula	$Cl_3(NCO)_3$	$NaCl_2(NCO)_3$	$NaCl_2(NCO)_3 \cdot 2H_20$
Molecular Weight	232	220	256
Color and Physical Form	White crystalline solid in regular, granular or extra granular grades		
Available Chlorine, %	>90	62.5	55.5
Assay, %	99	>97	>99
Cyanuric Acid, %	55.5	58.6	50.4
Inerts	<1	<3	<1
Melting Point, °C (with decomposition)	225	240	Loses 1 H_20 at >40 2 H_20 at >80 Decomp. 240
Loose Bulk Density: **(lb./cu.ft.)			
Regular:	66	-	-
Granular:	63	55	58
Extra Granular:	64	57	59
Solubility at 25° C (gm/100gm H_20)	1.2	24	28
pH, 1% Solution at 25°C:	3.0	6.0	6.0

* The above data are based on samples tested in the laboratory and are not guaranteed for all samples.

** 1gm/ml = 62.43 lb./cu. ft.

Table 2* Screening Characteristics of ACL® Chlorinated Isocyanurates

U.S. Standard Mesh Screens	ACL® 90 PLUS			ACL® 60		ACL® 56	
	R	G	XG	G	XG	G	XG
+10					2		
+12			1				2
+16		1					
+20	1			2		2	
+40		95	95	74*	96*	72*	99*
+60		99*	99*	98*	99*	90*	99.5*
thru 100	95*	0.5*	0.5*	2.0	2.0	2.0	2.0
+200	40-85						
thru 325	25*						

* typical value; not a specification.

Key:
R = regular (powder form)
G = granular
XG = extra granular

All values not otherwise specified are expressed as % cumulative retained by weight.

Properties of ACL® Chlorinated Isocyanurates

All the grades of ACL chlorinated isocyanurates are white, crystalline solids, The chlorinated-s-triazinetriones are commonly referred to as chlorinated (iso) cyanurates. ACL 90 PLUS may, therefore, be called trichloro(iso)cyanuric acid. ACL 60 is the sodium salt of dichloro(iso)cyanuric acid, and ACL 56 is the dihydrate of ACL 60. Since ACL 60 and ACL 56 are identical in chemical composition except for the presence of hydrate water in ACL 56, their chemical properties are virtually the same.

Chemical

ACL can be used to make safe and effective bleaching and sanitizing formulations. The recommended practice is to utilize formulations that dissolve rapidly in water. When dissolved in water, ACL will hydrolyze to form hypochlorous acid and cyanuric acid.

$ACL + H_20 \Rightarrow$ HOCl (hypochlorous acid) + Cyanuric acid

Hypochlorous acid is the material responsible for the bleaching and sanitizing actions of ACL. Cyanuric acid is the chlorine carrier.

When used as bleaching agents and sanitizers, the formulations should contain enough ACL to obtain hypochlorous acid concentrations (expressed in terms of available chlorine) of 50-200 ppm in water. **The preparation of concentrated solutions or slurries of ACL is not recommended.**

Solubility and pH

ACL properties are directly related to their chemical structures. The sodium atoms in ACL 56 and ACL 60 make these the most soluble (Table 1). Both of these dissolve very quickly in well agitated water. Although both give slightly acidic solutions, they do not significantly reduce the pH of the water. However, ACL 90 PLUS is more acidic and will lower the pH of water solutions. ACL 90 PLUS is also considerably less soluble, but can be made to dissolve very rapidly by raising the pH of the water above 9. ACL solubilities are increased significantly with higher water temperatures and pH (9 or more).

Chlorine value and effectiveness

ACL 90 PLUS has the highest available chlorine content of any solid chlorine-containing product in the marketplace. ACL 60 has the second highest chlorine content of the ACL family followed by ACL 56.

In water, all of the ACL products release their available chlorine very rapidly, even at low (4°C) temperatures. As a result, **all of the available chlorine is fully utilized, and the customer receives full chlorine value.** Other solid chlorine products are less effective because their chlorine is released too slowly. For this reason, the ACLs offer the highest and most effective chlorine values.

Stability

ACLs are stable for long periods of time when stored under cool, dry conditions. **Care should be exercised in selecting formulation ingredients.** Free moisture and incompatible materials should be avoided because they reduce ACL stability and lead to chlorine loss. Because ACL 90 PLUS is the least stable to adverse storage conditions or admixture with other chemicals, it should be formulated with anhydrous ingredients. **ACL 90 PLUS formulations should not contain alkaline components.**

Choice of ACL® in formulations

The choice of the particular composition and grade of ACL depends largely upon the type of application for which it will be used, the method of formulation, the other ingredients present and storage conditions of the finished product. ACL 90 PLUS is the most economical source of available chlorine, although its acidic nature makes it less compatible with the alkaline ingredients in a formulation. Formulations containing ACL 90 PLUS tend to have a more pronounced chlorine odor and are less stable under adverse storage conditions than those containing the salts of dichloro-s-triazinetrione. For these reasons, **only certain materials can be used with ACL 90 PLUS to produce stable formulations.** Granular ACL 90 PLUS is employed in industrial and institutional laundry bleach formulations (page 8) where stringent storage conditions are necessary.

ACL 56 and ACL 60 are more versatile and may be used for both household and industrial products. ACL 60 contains a higher level of available chlorine but both may be formulated to give stable finished products.

Chemical incompatibility

ACLs are very effective bleaches and sanitizers because they are highly reactive chemicals by virtue of their oxidizing characteristics. They can react with a variety of organic and inorganic chemicals that are prone to oxidation. To determine what chemicals are incompatible with ACL, refer to the section entitled “Chemicals Incompatible with ACL”, page 21.”

Reaction to heat

ACLs undergo decomposition when heated to temperatures above 200°C. ACL 60 continues to sustain thermal decomposition (fusion) throughout the entire mass even after removal of the heat source. ACL 56 is relatively more stable but, on prolonged heating, ultimately undergoes a similar decomposition after initial loss of the hydrate water at 40°C (100°F). The water liberated can cause lumping in containers, as well as caking and heat effects in formulations of ACL 56. ACL 90 PLUS decomposes on heating but does not sustain a fusion once the heat source is removed.

Reaction with water[1,2]

The preparation of concentrated solutions or slurries of ACL is not recommended. ACLs will partially decompose to form nitrogen trichloride (NCl_3), an explosive chemical with lachrymatory vapors. This reaction is especially hazardous with ACL 90 PLUS since large quantities of NCl_3 may be produced in a short period of time. With the other ACLs the formation of NCl_3 proceeds much more slowly and does not present the same degree of danger.

Applications of ACL®

Laundry bleach

ACLs are widely used as bleaching agents for cotton fabric in industrial and institutional dry bleach formulations. When formulated properly, they have a high solubility and a rapid rate of solution. The bleaching efficiency of these products is almost as high as that of the inorganic hypochlorites, such as sodium hypochlorite. ACLs however, cause less fabric damage than that produced by the inorganic-hypochlorites when accidentally spilled directly on fabric.

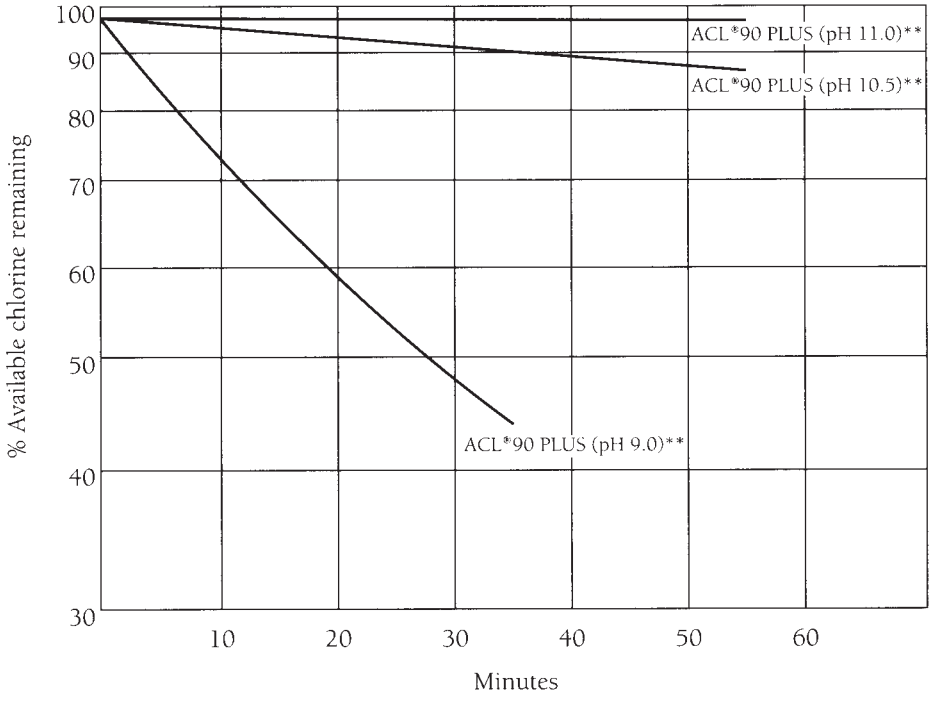
Bleaching conditions

Bleaching action generally takes place in solutions with pH levels of 10 to 10.5 at temperatures of 140-160°F (60-71°C) and at available chlorine levels ranging from 50 to 200 ppm for a period of about 10 minutes. The chlorine stability of ACL chlorinated-s-triazinetriones in solution is dependent on pH levels (Figure 1). Solutions with a pH level above 10 have good stability for at least the length of the entire bleaching process.

Figure 1 Relative Rates of Decomposition of ACL® 90 PLUS in Solution*

Original concentration of available chlorine = 600-630 ppm

Temperature 60°C+/-1°



* ACL 60 and ACL 56 give the same results
** These data are based upon samples tested in the laboratory and are not guaranteed for all samples.

Bleach formulations

Dry chlorine bleaches generally contain between 10% and 30% available chlorine. ACL may be formulated with, or used in conjunction with other components:

Builders: These ingredients are used to enhance the efficiency of soaps and detergents to overcome difficult washing conditions caused by heavy soil or hard water. Alkaline chemicals, such as sodium silicates, sodium hydroxide (caustic soda), sodium carbonate (soda ash) and sodium sesquicarbonate, are used to increase the pH levels and to improve cleaning performance. Sodium silicates provide the additional functions of soil suspension and corrosion inhibition. Sodium tripolyphosphate is used mainly as a water softening agent because of its excellent heavy metal sequestration properties. Most formulated laundry bleaches contain a combination of builders to suit a specific application.

Surfactants: These provide detergency in laundry operations. Anionic surfactants, such as the linear alkylbenzene sulfonates (LAS), are the most commonly used. Nonionic surfactants, such as the polyoxyethylated and polyoxypropylated glycols, also may be used for certain applications.

Other ingredients: In addition to builders and surfactants, a laundry operation also may utilize soil-suspending agents, such as carboxymethylcellulose, optical brighteners, bluing agents and fabric softeners.

While builders and other components do improve the overall performance of the formulations, such ingredients do not increase the bleaching potential of the chlorine compound.

Dry laundry bleach compositions containing ACLs are often simple products incorporating one other ingredient:

	Weight%
ACL® 90 PLUS**	15-35
Sodium sulfate	balance*

If packaged properly to exclude moisture and stored away from excessive heat, bleaches of this type are stable for long periods of time. Sodium sulfate is an inert ingredient. The ACLs are sometimes compounded with builders and other components. A basic formulation is shown below:

	Weight%
ACL® 56, or ACL® 60**	15-40
Sodium tripolyphosphate	30-40
Sodium silicate and/or caustic soda**	20-30
Anionic surfactants	0-3
Optical brighteners	0-0.3
Carboxymethylcellulose	0-1
Sodium carbonate, sodium sulfate	balance

* The term “balance” used in formulations throughout this text refers to the quantity of ingredient required to make up the formulation to 100% by weight.

** Manufactured by OxyChem.

Applications of ACL® (continued)

Bleach formulations (continued)

The ingredients of these formulations should be anhydrous to provide maximum chlorine stability of the product. Since some of the strongly alkaline chemicals, such as the sodium silicates and caustic soda, are very hygroscopic, **moisture should be avoided during manufacturing and storage.** Formulations of this type tend to have a shorter shelf life than those previously described.

Choice of ACL® in bleach formulations

All the grades of ACL (Table 1) produce excellent bleach products when properly formulated. ACL 90 PLUS is a good choice on a cost performance basis for most bleach applications incorporating an inert ingredient, such as sodium sulfate. Although the solubility of ACL 90 PLUS is considerably lower than that of ACL 60 and ACL 56, the high pH levels and water temperatures encountered in bleach solutions increase the solubility and rate of solution sufficiently to provide effective bleaching action.

ACL 90 PLUS is not, however, recommended for formulated bleaches containing strong alkali, surfactants or hydrated chemicals. These materials may react with ACL 90 PLUS causing decomposition of the triazine ring and leading to rapid gas evolution, creating a hazard of explosion.

ACL 60 and ACL 56 are much less reactive than ACL 90 PLUS and may be used in conjunction with builders, provided tests are performed to ensure chlorine stability and safety of the product prior to manufacture.

Machine dishwash detergents

ACLs are used in machine dishwash detergents for the home and for industrial and institutional (I&I) purposes. The **chlorine contributes to the overall cleaning power of the detergent** by oxidizing proteinaceous soil, leaving dishes shiny and reducing spots on glassware. Most dishwash detergents also contain the following components:

Sodium tripolyphosphate controls water hardness and enhances detergency.

Sodium Silicates provide alkalinity and soil suspension and prevent metal corrosion and filming of glassware.

Surfactants provide detergency and control foaming.

Fillers, such as sodium sulfate and sodium carbonate, balance the formulations.

Sodium carbonate is generally used when additional alkalinity is required to supplement that provided by the silicates. The use of **sodium chloride** is **not recommended** in machine dishwash products because the chloride ion may attack metals to cause pitting of silverware.

Household machine dishwash detergents

These products usually operate at lower pH and chlorine levels than the I&I products. With normal use concentrations of about 1.5-2.5% by weight of the detergent, the level of available chlorine in the wash solution is in the range of 30 to 40 ppm. The pH level of the solution should be above 10 to maintain adequate detergency but should be less than 11 to guard against effects of a highly caustic product. The temperature of the incoming water should be at least 120°F to ensure a rapid rate of solution of the detergent and satisfactory soil removal.

Formulations

A good machine dishwash detergent formulation should show adequate cleaning performance under less than ideal conditions of soil load, water temperature and water hardness. The composition of the detergent also may be subject to restrictions imposed by regulatory agencies, as in the case of phosphorus level. The heavy metal ions present in hard water interfere with the cleaning process.

As a general rule, the higher the level of water hardness, the greater will be the requirement for **sodium tripolyphosphate** to hold the metal ions in solution. The sodium tripolyphosphate present should be at least partially hydrated to allow for rapid solubility of the detergent and to minimize the problem of the detergent caking in the dispenser cup during the washing process. Anhydrous sodium tripolyphosphate is typically selected for an agglomerated detergent formulation while a partially hydrated sodium tripolyphosphate is usually selected for a dry blended detergent.

A **surfactant** with low-foaming properties should be used. The nonionic polyoxypropylene and polyoxyethylene glycols are the most suitable surfactants for this application. These products do, however, have the potential of reacting with some chlorine-releasing agents, but the interaction can be minimized by adsorbing the surfactants on to the alkaline ingredients prior to admixing ACL during manufacture.

The quantity and type of **sodium silicate** used will affect the pH and chlorine stability of the product. Sodium metasilicate, which has a SiO_2/Na_2O ratio of 1.0, is the most popular alkaline silicate used in this application. Anhydrous sodium metasilicate provides greater chlorine stability on storage than the pentahydrate form. Using the less alkaline hydrous polysilicates or liquid silicate solutions with $Si0_2/Na_20$ ratios of about 2.0 to 2.4 provides a product with a lower pH level and also contributes significantly to chlorine stability. Additional alkalinity may be provided by sodium carbonate. Trisodium phosphate (Na_3PO_4) or other orthophosphates are not recommended for this purpose as they form insoluble salts with calcium and magnesium ions present in water, thereby contributing to spotting of glassware and china.

The concentration of available chlorine in the formulation ranges from 0.5 to 1%. Low phosphate products generally contain higher chlorine levels to compensate for the decrease in cleaning efficiency due to the reduced amounts of sodium tripolyphosphate.

Machine dishwash detergents for household use are manufactured by two methods:

- dry blending
- agglomeration

Dry blend formulations are granular products with the following basic formulation:

	Weight%
Sodium tripolyphosphate	34-45
Water	4-10
Nonionic surfactant	1-3
Sodium carbonate	5-15
Sodium metasilicate*	10-15
ACL® 56 or ACL® 60*	1.5-2.5
Sodium sulfate (if required as filler)	balance

* Manufactured by OxyChem.

Formulations
(continued)

Mixing is generally accomplished in a ribbon, paddle or tumble type blender. The order of mixing of the components should be such that the nonionic surfactant is adsorbed onto the alkaline chemicals prior to addition of the ACL which should be added last.

Agglomerated formulations of machine dishwash detergents based on ACLs may have the following general composition:

	Weight%
Sodium tripolyphosphate	30-45
Nonionic surfactant	1-3
Sodium carbonate	10-25
Sodium silicate solution (40-50% solids)	20-30
ACL® 56 or ACL® 60	1.5-2.5
Sodium sulfate	balance

Agglomerated detergents are manufactured by a continuous process whereby the dry ingredients are mixed together and agglomerated by addition of a silicate solution. The water from this solution hydrates the alkaline ingredients, particularly the sodium tripolyphosphate, and a dry, granular product is obtained. Further processing such as conditioning, drying, milling and screening may be necessary to obtain a stable, free-flowing product of the required particle size and bulk density.

Select the ACL granulation to match the agglomerated base particle size and add near the final stages of the “conditioning” operation. By this means products of exceptional chlorine storage stability can be achieved.

Industrial and Institutional (I&I) machine dishwash detergents

I&I detergents are dry blended products which generally operate at higher pH and chlorine levels than household detergents to compensate for increased soil loads. Alkalinity may be achieved by sodium meta-silicate, sodium orthosilicate, caustic soda or soda ash, or combinations of these ingredients. The available chlorine content of the formulation may be between 2% and 4%. A basic formulation is given below:

	Weight%
Sodium tripolyphosphate	30-50
Sodium metasilicate/caustic	15-30
Nonionic surfactant	0-3
ACL®60	2-6
Soda ash	balance

Since products of this type are strongly alkaline and hygroscopic, they should be used within a few months of manufacture.

Cleaners and sanitizers

Cleaners and sanitizers find useful applications in the food processing industry, which includes dairies, breweries, meat packaging and soft drink manufacture. These products also are widely used in restaurants and cafeterias to wash equipment and surfaces used for food preparation and food service. Hospitals, hotels, motels and the janitorial trade are large users of cleaning products.

ACLs are used in a wide range of cleaners and sanitizers. The available chlorine is effective against odor and stains and aids in the removal of proteinaceous soil. In proper concentrations, these chlorine releasing agents also are effective germicides. Aqueous solutions of ACLs are equivalent in germicidal activity to sodium hypochlorite solutions at the same pH and chlorine levels. Changes in pH levels from 6 to 10 do not appreciably affect the germicidal activity of these products at normal use concentrations. In contrast, the organic chlorine sources currently available, such as the chloramines, drastically lose their **germicidal** efficiency at pH levels above 7.[3]

The FDA has approved the use of ACL for the preparation of sanitizing solutions on food-processing equipment and utensils and on other food contact articles,[4] as specified in the referenced section under Title 21 of the Code of Federal Regulations within the conditions prescribed. Any product labeled or intended for use as a disinfectant or sanitizer requires registration with the United States Environmental Protection Agency.

Cleaners and sanitizers based on ACLs usually contain the following other components:

Phosphates, such as sodium tripolyphosphate and tetrasodium pyrophosphate, are excellent builders suitable for most cleaning products. Sodium tripolyphosphate has a higher calcium sequestration capacity than tetrasodium pyrophosphate. Trisodium phosphate also may be used in some applications for alkalinity and buffering action although it has no sequestration properties to control water hardness.

Silicates, such as sodium metasilicate, are used in conjunction with the phosphates to provide alkalinity and soil suspension.

Surfactants are often employed to enhance detergency. The anionic or nonionic types may be used depending upon the type of formulation characteristics desired. For inplace cleaning, the surfactant is generally excluded to avoid foaming.

Acid salts, such as sodium acid sulfate and sodium acid phosphates, are generally used in certain hard surface cleaners to remove stains and other deposits. Typical applications incorporating acid salts are toilet bowl cleaners and metal cleaners.

Alkali salts, such as soda ash, may be used when added alkalinity is desired.

Neutral salts, such as sodium chloride and sodium sulfate, are inert substances normally used as fillers.

Applications of ACL® (continued)

Cleaner and sanitizer formulations

Cleaning and sanitizing products contain varying amounts of available chlorine and other components, depending upon the applications for which they are formulated. The compositions given below are suggested only as a basic guideline. A variety of products may be formulated for household or industrial use incorporating these ingredients or other suitable chemicals in appropriate concentrations for different applications. As a service to our customers, OxyChem has developed the sanitizer and cleaner formulations listed below. Customers interested in marketing a product similar to those listed below should contact OxyChem technical service.

Sanitizers

A sanitizer claim may be made for a product only if the use concentration of available chlorine can be shown to provide germicidal action. Sanitizing solutions are generally applied to previously cleaned surfaces to reduce bacterial count. A dry sanitizer is diluted at point of use with a sufficient quantity of water to provide the desired level of available chlorine in solution. The amount of sanitizer and water to use to obtain a given available chlorine level, usually 100 ppm, is specified in the use directions on the product label.

The formulations shown below are typically used in the home, dairies, breweries, hospitals, restaurants and food processing plants to sanitize hard (non-porous) surfaces such as dishes, glasses, utensils, food processing equipment, floors and walls which have food stains. The fabric and diaper sanitizer is specially formulated to remove stains and reduce ammonia causing bacteria in the institutional and commercial laundering of fabrics and diapers.

Detergent Sanitizer	Weight%
ACL® 56	6
Sodium Tripolyphosphate	36
Sodium metasilicate	8
Sodium sulfate	50
Available chlorine	3.3

Fabric and Diaper Sanitizer	Weight%
ACL® 56	18
Sodium tripolyphosphate	20
Sodium dodecyl benzene sulfonate	3
Sodium sulfate	34
Sodium carbonate	25
Available chlorine	10

Alkaline Sanitizer	Weight%
ACL® 56	25
Sodium tripolyphosphate	10
Sodium sulfate	65
Available chlorine	13.9

Sanitizers
(continued)

Acidic Wash Sanitizer	Weight%
ACL® 56	28
Sodium sulfate	42
Monosodium phosphate	30
Available chlorine	15.5

Mildly Acidic Wash and Surface Sanitizer*	Weight%
ACL® 56 or ACL® 60	34
Sodium sulfate	66
Available chlorine	19-21

Wash and Surface Sanitizer*	Weight%
ACL® 56	40
Sodium sulfate	60
Available chlorine	22

Scouring powders

The presence of chlorine-releasing agents improves the cleaning performance of scouring cleansers. Oil film, food and stains are readily oxidized by chlorine to soluble components which can be rinsed off with water. The anionic surfactant further contributes to detergency by its wetting and foam-suspending action.

The largest component of the formulation is silica flour, feldspar or another inert ingredient to provide scouring action. A basic formulation is given below:

	Weight%
ACL® 56, ACL® 60 or ACL® 90 PLUS	1
Trisodium phosphate or soda ash	3-5
Anionic surfactant	2-5
Silica flour	balance

Scouring cleansers of this type may be used for household or industrial purposes. If a phosphate-free product is required, the trisodium phosphate may be replaced by soda ash in appropriate formulations.

* Most commonly registered formulations

Toxicity

ACLs are considered to be no more than slightly toxic by ingestion in single doses and by single dermal applications. The ACL products are considered to be moderately to severely irritating to intact and abraded rabbit skin.

The products were found to be corrosive when approximately 0.1 ml by volume of powdered sample was placed into the conjunctival sac of the rabbit eye. Irreversible damage was observed 10-14 days after instillation of the sample. ACL is, therefore, considered to be corrosive to rabbit eyes.

	Acute Oral LD in rats, mg/kg	Dermal LD in rabbits, mg /kg
ACL® 56	620	11,000
ACL® 60	700	6000
ACL® 90 PLUS	600	7,600
Cyanuric acid	>10,000	>7,940

Fish toxicity studies show that ACL possesses a relatively high order of toxicity to fingerling rainbow trout and bluegill sunfish because of its available chlorine content. In contrast to the chlorine in ACL, the cyanuric acid portion of the molecule is essentially non-toxic. It is the cyanuric acid portion of the molecule which persists after the chlorine acitivity has been discharged by chemical reaction with an oxidizable substance.

Safety, Storage, Handling and Disposal

Refer to the Material Safety Data Sheets of the ACL products and the industrial safety bulletin cited in reference 6 (page 26) for further information on safety, storage and handling.

ACLs are strong oxidizing agents, hence their storage conditions should comply with the codes established by 1: Article 80 uniform fire code, International Fire Code Institute, Whittier, California and 2: NFPA 430, National Fire Protection Association, Quincy, Massachusetts. Since both codes are used throughout the U.S., consult with local fire departments to determine which code applies. General guidelines for storage are given below.

ACL should be stored in a cool (temperatures not to exceed 125°F for 24 hours), dry, well-ventilated area, segregated from incompatible chemicals. ACL product containers should be stored on pallets and stacked according to OxyChem's recommendations. Provisions should be made to open and use ACL containers in well-ventilated work areas to protect handlers from excessive chlorine odor and dust. Good housekeeping practices are essential for safe storage and handling.

ACL 90 PLUS can be stored with or without a sprinkler system, according to both of the above fire codes. It does, however, present an explosion hazard when wet. For this reason it should be segregated from ACL 60 and ACL 56 which are capable of sustaining fusion.

The DOT classifies ACL 60 and ACL 90 Plus as oxidizers. ACL 56 and ACL 90 Plus are classified as Class 1 oxidizers by the NFPA. ACL 60 is classified as a Class 3 oxidizer by the NFPA. On sustained application of heat, ACL 56 loses its water of hydration and then follows the same decomposition pattern as ACL 60. Guidelines for the storage of ACL 60 and ACL 56 are given in both fire codes.

Personnel safety

Eye Protection:
Wear chemical splash goggles and have eye baths immediately available where there is potential for eye contact. ACL products are corrosive to the eyes.

Skin Protection:
Wear appropriate protective gloves and protective clothing that provide a barrier to prevent skin contact. Consult glove manufacturers to determine appropriate type glove for a given application. Wash immediately if skin is contaminated. Launder contaminated clothing and clean protective equipment before reuse. Provide a safety shower at any location where skin contact can occur. Wash thoroughly after handling. ACL products are irritating to the skin.

Respiratory Protection:
Avoid breathing dust or vapor. Use NIOSH/MSHA approved equipment when airborne exposure limits are exceeded. Full facepiece equipment is recommended and, if used, replaces need for face shield and/or chemical splash goggles. Consult respirator manufacturer to determine type equipment for given application. The respirator use limitations specified by NIOSH/MSHA or the manufacturer must be observed. High airborne concentrations may require use of self-contained breathing apparatus or supplied air respirator. Respiratory protection programs must be in compliance with 29 CFR 1910.134.

Safety, Storage, Handling and Disposal (continued)

Personnel safety
(continued)

Ventilation:
Provide ventilation to control exposure levels below airborne exposure limits. Use local mechanical exhaust ventilation at sources of air contamination such as open process equipment.

Airborne Exposure Limits[5]:
The Occupational Safety and Health Administration (OSHA) and the American Conference of Governmental Industrial Hygienists (ACGIH) have not established specific exposure limits for these materials. However, the exposure limits for chlorine have been established as follows.

Chlorine

OSHA PEL/8 hr. TWA:	0.5 ppm (1.5 mg/m^3)
OSHA PEL/15 min. STEL:	1 ppm (3mg/m^3)
ACGIH TLV/8 hr. TWA:	0.5 ppm (1.5 mg/m^3)
ACGIH TLV/15 min. STEL:	1 ppm (3 mg/m^3)

PEL —permissible exposure limit
TLV —threshold limit value
TWA —time weighted average
STEL —short time exposure limit

Emergency and First Aid Procedures:
If swallowed, drink large amounts of water. DO NOT induce vomiting. Avoid alcohol. Call a physician or poison control center immediately.

For eye: the object is to flush material out immediately, then seek medical attention. Immediately flush eyes with large amounts of water for at least 15 minutes, forcibly holding the lids apart to ensure complete irrigation of all eye and lid tissue. Washing the eye within one (1) minute is essential to achieve maximum effectiveness. SEEK MEDICAL ATTENTION IMMEDIATELY.

For skin: Immediately brush off the excess chemical and flush with plenty of water. Remove contaminated clothing. Wash clothing before reuse. GET MEDICAL ATTENTION if irritation persists.

If inhaled: Remove to fresh air. If breathing is difficult, have trained person administer oxygen. If respiration stops, give mouth-to-mouth resuscitation. GET MEDICAL ATTENTION.

Note to physician: Probable mucosal damage may contraindicate the use of gastric lavage.

In case of fire or smoke: Call the fire department. Do not attempt to extinguish the fire without a self contained breathing apparatus (SCBA). Do not let the fire burn. Flood with copious amounts of water. DO NOT use ABC or other dry chemical extinguishers, since there is the potential for a violent reaction.

In case of contamination or decomposition: Do not reseal container. Follow disposal directions provided on the following pages.

Equipment

Conventional mixer types can be used for the formulation of these products but should be designed or modified to minimize attrition, dusting or spilling. Provision should be made to collect any dust from the mixer in a suitable dust-collecting system. Note, the dust collection system for ACL products should not be used to collect dust from materials that will react with ACL products. All equipment should be thoroughly cleaned before and after mixing to prevent the possibility of undesired reactions

Spill, leak and disposal

or fire as a result of accidental contamination. Due to the thermal decomposition properties of ACL 60, friction-producing equipment, such as screw conveyors or items with internal bearings, should be avoided whenever possible.

Emergency Spill and Leak Information:
Contain spilled material. Any spillage of ACL products should be cleaned up as soon as possible to prevent contamination with foreigh materials with which it may react. Floor sweeping compounds should not be used.

KEEP SPILLED MATERIAL DRY. If allowed to stand in damp or wet areas, tear-producing vapors may result.

Keep unneutralized ACL out of sewers, watersheds and water systems.

Using clean, dedicated equipment, sweep and scoop up all spilled material, contaminated soil and other contaminated material and place into clean dry containers for disposal. Complete cleanup on a dry basis if possible. Sweeping compounds or other contaminants should not be mixed with ACL during this cleanup operation as fuming, fire or explosion may result. Follow all protective measures indicated in the “Personnel Safety” section of this document.

Spill Reporting:
Although ACL Chlorinated Isocyanurate has not been assigned a CERCLA RQ, the State may have more stringent reporting requirements. Also, if an ACL Chlorinated Isocyanurate spill gets into the ground or surface water, or is involved in a fire, chlorine containing gases may be released; therefore, the spill should be reported. It is best to report a spill if there is any uncertainty.

Disposal Information:
Dispose of in accordance with all applicable local, state and federal laws and regulations.

Wastes of this pesticide may cause irreversible eye damage and burns to skin and may be dangerous. Improper disposal of excess pesticide, spray mixture or rinsate is a violation of federal law. If these wastes cannot be disposed of by use according to label instructions, contact your State Pesticide or Environmental Control Agency, or the Hazardous Waste representative at the nearest EPA regional office for guidance.

Completely empty drum liner by shaking and tapping sides and bottom to loosen clinging particles. Empty residue into application equipment. Dispose of liner in a sanitary landfill by incineration as allowed by state and local authorities. If the container is contaminated and cannot be reused, triple rinse and dispose of in the same manner.

Do not dispose of filled or partially filled containers in a common waste compactor. Contaminants in the compactor, such as oil, sawdust, floor-sweeping compound, etc., could cause spontaneous decomposition of the material at ambient temperatures resulting in rupture of the drum and fire.

Dry material can be disposed of by incineration and/or by the chemical dechlorination/neutralization procedure described on the following page.

Dispose of **wet** material immediately. Do not transport or put into sealed containers. The chemical dechlorination/neutralization procedure described on the following page is recommended for disposal.

ACL® Waste Neutralizing Procedure

This procedure can be used to dechlorinate and neutralize small and large quantities of waste ACL products **only where such treatment is in compliance with Federal, State and local regulations.** The procedure should be carried out according to the instructions given below.

Site

A well-ventilated room or an outdoor location.

Equipment

Dechlorinating Vessel

- adequate capacity (5 gallons of water per pound of waste ACL)
- buckets, drums or tanks with proper structural design (with open top) and strength — especially large permanent structures and materials of construction (plastic, steel or fiberglass)

Agitator

- suitable size and capable of stirring the water vigorously

Chlorine Test Kits

- range - 0 to 3000 ppm

pH Meter

Protective Clothing/Equipment

- respirator
- goggles or face mask
- gloves

Materials

ACL Waste

- powder
- ground tablets

Liquid Caustic Soda (50% sodium hydroxide)

- Approx. 2.25 lbs per lb of waste ACL 90
- Approx. 1.52 lbs per lb of waste ACL 56 or ACL 60

or

Soda Ash (sodium carbonate)

- Approx. 2.5 lbs per lb of waste ACL 90
- Approx. 1.66 lbs per lb of waste ACL 56 or ACL 60

Sodium Sulfite

- Approx. 0.02 lb (0.33 oz) per 1000 ppm of chlorine per gallon

Process description

This process involves the addition of waste ACL products to alkaline aqueous solutions maintained at a pH of 10.5. At this pH, the major fraction of chlorine is destroyed by chemical reactions between chlorine and cyanuric acid contained in the waste ACL. As shown in the chemical reaction section below, the reaction results in the formation of nitrogen, sodium chloride, sodium carbonate and sodium cyanurate. This reaction occurs very rapidly and free chlorine decreases to a low level within about 2 1/2 hours. The remaining chlorine is then reduced to zero with the recommended amounts of sodium sulfite. The pH is then reduced to the appropriate level with acid.

Chemical reactions

Example: Dechlorination of ACL 90 ($C1_3N_3C_30_3$) with soda ash
3 $C1_3N_3C_30_3$ + Na_2C0_3 + 12 H_20—->
22 $NaHC0_3$ + 3 N_2 + 9 NaC1 + $NaH_2N_3C_30_3$

Note: $NaH_2N_3C_30_3$ = sodium cyanurate

Procedure

1. Fill the container with the appropriate volume of water. Be sure that the water fills only about 90% of volume of the container.
2. With the agitator on, add sufficient soda ash (or liquid caustic soda) to obtain a pH of 10.5.
3. Add the appropriate amount of waste ACL to the alkaline solution over a period of 5-10 minutes.
4. Check the pH every 30 minutes. If below 10, add enough soda ash (or caustic soda) to raise it to 10.5. If above 11, reduce the pH to 10.5 with muriatic or sulfuric acid.
5. Determine the chlorine level in about 2 1/2 hours. If <3,000 ppm, add the appropriate amount of sodium sulfite. If not, wait about 30 minutes then determine if the chlorine is below the indicated value, then add the appropriate amount of sodium sulfite.
6. Determine if the chlorine level has fallen to zero. If not, add more sodium sulfite.
7. Reduce the pH to the level required by the local regulations.
8. Dispose of waste solution in accordance with any environmental regulations.

Container handling and storage

Do not contaminate water, food or feed by storage or disposal.
Storage: Keep material dry and in a dry area. Store in original container where temperatures do not exceed 125°F. (52°C) for 24 hours. Retie polyethylene liner after each use and keep container tightly closed.

Container Disposal: Returnable metal container. Vacuum empty the container then return for reuse. If container is not reusable, vacuum or triple rinse. Then offer for recycling or reconditioning, or puncture and dispose of in a sanitary landfill, or by other procedures approved by state and local authorities.

Plastic Bulk Bag: Completely empty the bag into application equipment. Then dispose of empty bag in a sanitary landfill or by incineration, or, if allowed by state and local authorities, by burning. If burned, stay out of smoke.

Fiber Drum: Completely empty liner by shaking and tapping sides and bottom to loosen clinging particles. Empty residue into application equipment. Then triple rinse and dispose of liner in a sanitary landfill or by incineration as allowed by state and local authorities. If drum is contaminated and cannot be reused, dispose of in the same manner.

Plastic Pail: Triple rinse (or equivalent). Then offer for recycling or reconditioning, or puncture and dispose of in a sanitary landfill, or incineration, or, if allowed by state and local authorities, by burning. If burned, stay out of smoke.

Chemicals incompatible with ACL®

ACLs are highly reactive oxidizing and chlorinating agents. Precautions should be taken to prevent the mixing of these products with other incompatible chemicals during storage, handling and manufacture. Some of the chemicals incompatible with ACLs are listed below:

Acetic acid and acetic anhydride
Alcohols (methyl, ethyl and higher alcohols)
Aliphatic and aromatic unsaturated compounds
Amides
Amines
Ammonia and ammonium salts ("quats")
Biuret
Calcium hypochlorite
Dimethylhydrazine
Ethers
Fungicides
Glycerin
Oils and greases
Paint
Peroxides (hydrogen, sodium, calcium peroxide, etc.)
Peroxygen compounds
Perborates, percarbonates, perphosphates, persulfates
Petroleum products (gasoline, kerosene, etc.)
Phenols
Solvents (toluene, xylene, turpentine, etc.)
Some surfactants
Sulfides, sulfites, bisulfites, thiosulfates, nitrites and other reducing agents
Sweeping compounds
Urea

ACL in the presence of ammonia gas or aqueous solution of ammonia will generate hazardous amounts of $NC1_3$.

Hydrogen peroxide may react violently with ACL with liberation of oxygen.

Contamination with oils and greases may cause decomposition of ACL with formation of $C0_2$, $C1_2$, etc.

Concentrated solutions or slurries of ACL 90 PLUS greater than 0.1% (1,000 ppm) should never be prepared since large amounts of nitrogen trichloride may be formed.

ACL 90 PLUS is generally more reactive than the dichloro-s-triazinetrione salts, due to its greater solubility in organic media. Reactions of ACL 90 PLUS with some commonly used chemicals are given below:

Calcium hypochlorite: ACL 90 PLUS may form an explosive mixture with calcium hypochlorite.

Soda ash (Na_2C0_3): In a formulation containing ACL 90 PLUS as the major component, alkaline materials, such as soda ash, in the presence of moisture may cause decomposition, particularly if the pH is in the range of 8 to 9.

Turpentine: ACL 90 PLUS reacts almost explosively with turpentine, a highly unsaturated hydrocarbon.

Alcohols: ACL 90 PLUS mixed with lauryl alcohol (C_{12}) at room temperature will remain latent for a few minutes and then react vigorously with flame and black smoke. Rate of reaction with other alcohols varies with structure.

Ethers: A diethyl ether solution of ACL 90 PLUS containing a trace of alcohol or water will rapidly deposit cyanuric acid, probably with formation of the chlorinated ether.

Nonionic surfactants*: The nonionics are a combination of alcohols and ethers and can be rapidly reactive with ACL 90 PLUS. The reaction products of ACL 90 PLUS and nonionics are cyanuric acid and the chlorinated or oxidized nonionic. The reaction is probably similar to the reaction with ether above.

Toluene, xylene: ACL 90 PLUS heated in xylene or toluene will react to form the chlorinated organic and cyanuric acid. Chlorination probably occurs on the side chain. Reactivity with benzene is only slight.

Urea, biuret: ACL 90 PLUS will react with urea to form the chlorinated urea which subsequently breaks down to $NC1_3$ and $C0_2$. This is a very dangerous reaction because of the explosiveness of $NC1_3$. In alkaline solution, ACL reacts with biuret to form N_2, carbonate ion, etc.

Amides, sulfonamides: ACL 90 PLUS will chlorinate other amides in which the affinity of nitrogen for chlorine is greater than that of ACL 90 PLUS, e.g., in solution ACL 90 PLUS will react with toluene sulfonamide, benzene sulfonamide, dimethylhydantoin, glycoluril, etc., to form the corresponding N-chloro derivatives.

* Note: The nonionic surfactants are generally safe to use with the other grades of ACL when formulated appropriately.

Nitrogen Trichloride Formation

Nitrogen trichloride formation

As indicated on page 6 (“Reaction with water”), nitrogen trichloride can be formed from ACL particularly ACL 90 PLUS. Nitrogen trichloride (NCl_3) is a potentially hazardous chemical. Therefore, proper precautions should be taken to prevent its formation.

Nitrogen trichloride properties

Mol. Wt.	120
Specific Gravity	1.65
Melting Point	-40°C
Boiling Point	70°C
Appearance	A yellow, oily liquid or vapor
Solubility	About 0.2% in water at 25°C
Vapor Pressure	150 mm Hg at 20°C

Explosion characteristics

Any quantity of NCl_3 is potentially explosive and, therefore, under certain conditions, hazardous.

Liquid—Liquid NCl_3 will explode in contact with certain organic impurities, when melting after having been frozen, from impact or supersonic vibration, or on heating to 60°C or above.

Any conditions which allow NCl_3 to form and collect as a liquid are extremely hazardous.

Vapor—NCl_3 vapors can be exploded or decomposed (to N_2 and Cl_2) when concentrations in air are as low as 0.3%. At this low concentration, however, the propagation rate is extremely slow, on the order of several minutes per foot. At concentrations of 3-4%, the detonation is explosive with an instantaneous pressure rise. In general, 1-2% is considered a safe upper limit. There are no good data on what temperature or conditions are required to explode the gas. It is known that NCl_3 vapor (or vapor-air mixture) can be exploded by a spark or by temperature in excess of 100°C.

Thermal decomposition of ACL®

While the chlorinated-s-triazinetriones are generally non-flammable, decomposition of the triazine ring may occur at temperatures over 200°C. The decomposition provides sufficient heat to ignite paper, wood, product drums and other flammable material. Decomposition may be initiated by contact with a lighted cigarette, a hot welding rod or friction caused by metal-to-metal contact in equipment. A fusion may start at temperatures well below 200°C and perhaps even at ambient temperature if the product is contaminated with an easily oxidizable material, such as gasoline, oil, grease, sawdust, floor sweepings and strong alkali.

Labeling, Packaging, Shipping

Acceptable storage stability for products formulated with ACL chlorinated isocyanurates can be achieved if certain guidelines are observed. Please consult with OxyChem for the latest guidelines.

Formulations of materials in combination with other ingredients should be examined for conformance to federal, state and local regulations concerning product labeling. Labels should include precautionary information describing potential product hazards and give recommended practices for safe handling, storage and use.

Exclusion of moisture is the main criterion for designing a container for a finished formulation containing ACL. Bulk formulations may be stored in fiber drums with a polyethylene bag liner. Additional product stability, especially for formulations containing ACL 90 PLUS, may be provided by using an aluminum foil liner and a suitable desiccant in the product drum.

Practical moisture-resistant packages for household product include polyethylene or chipboard containers and cartons with a moisture barrier, foil laminate or overwrap.

[ACL 60 and ACL 90 PLUS require the Department of Transportation yellow label for oxidizing materials. **ACL is not shipped with other chemicals with which it is likely to react.]**

Analytical Method for the Determination of Available Chlorine*

The available chlorine contents of formulations containing ACLs is determined by an iodometric titration with sodium thiosulfate to a starch end point.

Reagents required:
Standard sodium thiosulfate solution 0.1N
Potassium iodide solution 10% by weight
Sulfuric acid solution 1:1 by weight
Starch indicator

Method:
A weight of sample, enough to give a sodium thiosulfate reading of at least 20 ml., is dissolved with stirring in about 200 ml. of distilled water in an Erlenmeyer flask. 10 ml. each of potassium iodide and sulfuric acid solutions are then added and the liberated iodine titrated with thiosulfate using starch as the indicator.

$$\% \text{ available chlorine} = \frac{\text{ml. thiosulfate} \times \text{N thiosulfate} \times 0.03545 \times 100}{\text{wt. of sample}}$$

Caution:
1. In highly alkaline formulations, an additional quantity of H_2S0_4, may be necessary to obtain an overall acid pH in the solution.

2. If carbonate is present in the formulation, the acid should be added slowly in order to prevent an excessive rate of $C0_2$ evolution.

3. Nonionic surfactants of the type present in machine dishwash detergents may interfere with the titration. The addition of a suitable solvent to the solution just prior to titration results in much sharper end point.

* see ASTM method D-2022 for more detailed information.

References*

1. J. E. O'Brien, "Equilibria in Aqueous Solutions of Chlorinated Cyanurates," *Chemical Water Supply Treatment District Symposium*, 1973, Editor A. J. Rubin, Ann Arbor Science, Ann Arbor, Michigan.

2. G.D. Nelson, "Equivalency of the Chlorinated-s-triazinetrione Products at Use Levels." Monsanto Company Report No. 8364, May 10, 1976, St. Louis, Missouri.

3. L. F. Ortenzio and L. S. Stuart, "The Behavior of Chorine-bearing Organic Compounds inthe A.O.A.C. Available Chlorine Germicidal Equivalent Concentration Test, "Journal of the Association of Official Agricultural Chemists, Vol. 42, 630-633, (1959).

4. Code of Federal Regulations Title 21—Food and Drugs—178.1010, "Sanitizing Solutions."

5. "TLV's Threshold Limit Values for Chemical Substances and Physical Agents in the Working Environment with Intended Changes for 1983-84," published by the American Conference of Governmental Industrial Hygienists (ACGIH), 6500 Glenway Avenue, Cincinnati, Ohio.

6. "Guidelines for Safe Handling and Storage of Calcium Hypochlorite and Chlorinated Isocyanurate Pool Chemicals," bulletin published by the Chlorinated Pool Chemicals Panel,** Chemical Manufacturers Association, Washington, D.C.

* Oxy Chem purchased the ACL business from the Monsanto Company on December 30, 1992. Therefore, many of the cited references are Monsanto technical reports.

** The Chlorinated Pool Chemicals Panel is comprised of representatives of all of the chlorinated isocyanurate producers and the major calcium hypochlorite producers of the world. The Chemical Manufacturer's Association serves as the administrator for this industrial safety committee.

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